A Century of Sapphire Crystal Growth

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ABSTRACT

Abstract: In Paris around 1890, A. V. L. Verneuil developed a flame fusion process to produce ruby and sapphire. By 1900 there was brisk demand for ruby manufactured by Verneuil's method, which was used with little alteration for 50 years. From 1932-1953, S. K. Popov in the Soviet Union established a capability for manufacturing high quality sapphire by the Verneuil process. In the U.S., under government contract during World War II, Linde Air Products Co. implemented the Verneuil process for making jewel bearings for precision instruments. In the 1960s and 1970s, the Czochralski process was implemented by Linde and its successor, Union Carbide, to make higher quality crystals for ruby lasers. Stimulated by a government contract for structural fibers in 1966, H. LaBelle invented edge-defined film-fed growth (EFG). The Saphikon company, owned now by Saint-Gobain, evolved from this effort. Stepanov independently developed edge-defined film-fed growth in the Soviet Union. In 1967 F. Schmid and D. Viechnicki at the Army Materials Research Lab grew sapphire by the heat exchanger method (HEM). Schmid later established Crystal Systems, Inc. around this technology. Rotem Industries, founded in Israel in 1969, perfected the growth of sapphire hemispheres and near-net-shape domes by gradient solidification. In the U.S., growth of near-net-shape sapphire domes was demonstrated by both the EFG and HEM methods in the 1980s but neither method became commercial. Today, domes in the U.S. are made by "scooping" sapphire boules with diamond-impregnated cutting tools. Commercial markets for sapphire, especially in the semiconductor industry, are healthy and growing at the dawn of the 21st century.

Introduction and Prehistory

Commercial production of synthetic sapphire is now 100 years old.[1] Sapphire is a readily available crystal product used as an optical window for industrial and military applications in which the window must withstand extreme environments. Sapphire transmits from the ultraviolet through the visible and into the midwave (3-5 μm) infrared regions. It withstands high temperature, rapid heating and cooling, high pressure, and resists chemical corrosion. Sapphire is the abrasion-resistant window in bar code scanners and the scratch-proof crystal face of expensive wristwatches. High crystal perfection, low reactivity, and appropriate unit cell size make sapphire an excellent substrate in the semiconductor industry for blue light-emitting diodes

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and diode lasers. Sapphire is also used for equipment to manipulate semiconductor wafers during processing in extreme environments. Sapphire and its cousin, ruby, are employed as jewel bearings in precision mechanical instruments.

Sapphire is also known as corundum, the natural crystal of aluminum oxide, Al_2O_3 (Figure 1). It is stable up to its melting temperature of 2050ºC. Its hardness of 9 on the Mohs mineral scale is second only to that of diamond. The 3-fold symmetry axis of the trigonal crystal, designated *c*, is also called the optical axis. Two-fold symmetry axes designated *a* and *m* are found perpendicular to the 3-fold axis. Pure corundum is clear and colorless. Natural sapphire has a variety of colors. Blue sapphire contains iron and titanium impurities whose charge transfer transition ($Fe^{2+},Ti^{4+} \rightarrow Fe^{3+},Ti^{3+}$) absorbs red light and imparts blue color to the crystal.[2] The red color of ruby comes from Cr^{3+} in corundum, which gives rise to electronic transitions that absorb visible light.

Figure 1: Natural sapphire (1, 2), natural ruby (3), and synthetic sapphire (4, 5).

Early in the 19th century, it was thought that sapphire and ruby were oxides of the elements aluminum and silicon.[1] In 1817, J. L. Gay-Lussac found that pure aluminum oxide (also called alumina) could be prepared by thermal decomposition of ammonium alum, $(NH_4)Al(SO_4)_2 \cdot 12H_2O$. Alumina prepared by this route remains as the raw material for making sapphire today. In 1840 H. Rose showed that silicon observed in sapphire was an impurity introduced from the agate mortars used to grind sapphire for chemical analysis. Once the true composition of sapphire was known, many chemists sought to make the valuable crystal. In the period 1837-1840, H. Gaudin used a torch to fuse alumina prepared from ammonium alum to prepare small hexagonal platelets of corundum. Mixing alum with chromium salts prior to fusion produced small, strained, hard red particles whose density was less than that of natural ruby because of trapped gas. Gaudin believed he had made a glass, but modern work suggests that he made crystalline ruby.[1] In 1851, H. Senarmont made microscopic rhombohedral crystals by heating solutions of aluminum chloride to over 350ºC in sealed tubes. In 1848, J. J. Ebelman prepared ruby by fusing alumina and boric acid with chromium oxide. Ebelman and F. Parmantier prepared crystals from alumina dissolved in fused salts at high temperature. Other investigations were carried out by R. Boettger, W. Bruhns, A. Brun, H. Debray, H. St.-C. Deville, H. Caron, Daubré, C. Doelter, L. Elsner, G. Friedel, H. Grandeau, P. Hautefeuille, M. Houdard, H. Loyer, J. W. Mallet, G. Medanich, S. Meunier, H. Moissan, J. Morozewicz, C. F. W. A. Oetling, H. Perrey, L. Schuch, and E. Weinschenk.[1,3,4] None of this work produced more than microscopic crystals.

More successful investigations were led by Edmond Frémy (1814-1894) at the Museum of Natural History in Paris.[1] Frémy and his assistant, Charles Feil, published a paper in 1877 in which they obtained small, clear, red ruby crystals. Fireclay crucibles with 20-kg charges were held at red heat for periods up to 20 days. Lead oxide (Pb_3O_4) was converted to lead aluminate, which reacted with silica to give lead silicate plus corundum. Ruby was obtained by adding 2-3 wt% potassium dichromate to the reaction. After Feil died in 1876, Frémy's new assistant was Auguste V. L. Verneuil (1856-1913), who had applied to work with Frémy at the age of 17. Clear

ruby crystals up to 3 mm in diameter and 0.3 carat in mass (1 carat = 0.2 grams) were grown from alumina in a potassium hydroxide/barium fluoride flux in a ceramic crucible at 1500ºC. In unsuccessful attempts to increase the size of the ruby crystals, flux growth was scaled up at the Saint-Gobain glass factory and then in 50-liter crucibles at the Appert glass factory. Although Frémy thought he was crystallizing alumina from the flux, Kurt Nassau[1] suggests that alumina and barium fluoride give gaseous aluminum fluoride. Aluminum fluoride reacts with water vapor that diffuses through the porous crucible to give alumina, which crystallizes in many locations with little chance to grow into larger crystals. Frémy summarized his investigations in a book in 1891.[5] He retired in 1892 and died in 1894. Figure 2, reproduced from Nassau,[6] was taken from Frémy's book.
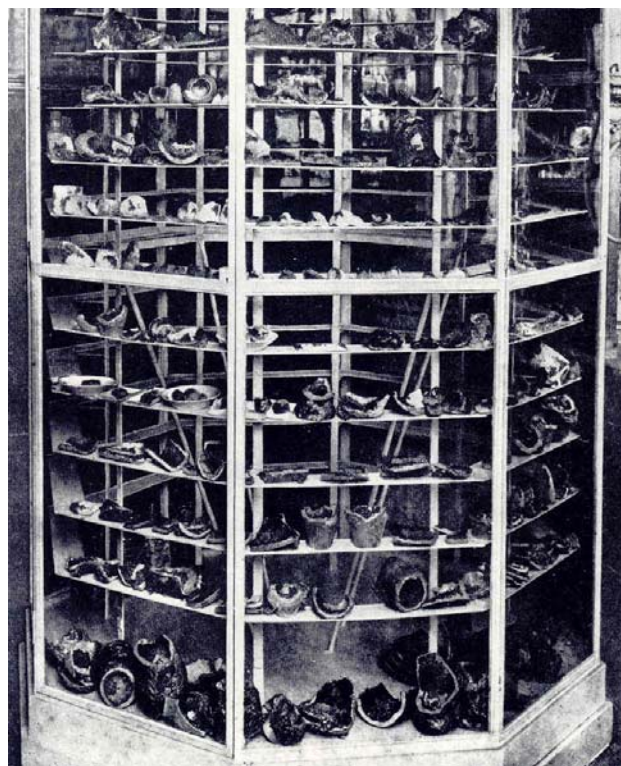

Figure 2: Crystal growth storage cabinet from Frémy's lab.[5,6]

Flame Fusion and the Verneuil Process

In 1885 rubies selling for $1000-2500 per carat from an unknown source appeared in Geneva and were purported to be natural gems.[1] Investigation of the crystals at the Sorbonne in Paris and at Tiffany in New York found microscopic gas bubbles suggestive of a high-temperature synthetic process. The French Syndicate of Diamonds and Precious Stones ruled that the crystals had to be marketed as "artificial," which reduced their price to $25-40 per carat. Modern investigation of "Geneva" rubies by Nassau suggests a 3-stage flame fusion synthetic process.[1] In the first stage, alumina plus a chromium salt are fused on a ceramic support to form a tiny crystalline ball. The ball is then turned upside down and growth of a larger crystalline ball is continued by adding fresh material to the flame. The final stage appears to require 2 torches to enlarge the growing crystal to its final dimensions. The proposed mechanism is supported by 2 discontinuities in chromium concentration inside "Geneva" rubies. One of the people who examined "Geneva" ruby in 1886 was the mineralogist, P. M. E. Jannettaz at the Museum of Natural History in Paris. He concluded that fusion was involved in the creation of the "Geneva" ruby and he discussed his findings with his colleague, Verneuil.

While working with Frémy, Verneuil had earned his bachelor, masters, and doctoral degrees. When Frémy retired in 1892, Verneuil became professor of applied chemistry at the Museum of Natural History in Paris. In 1886, following his introduction to the "Geneva" ruby by Jannettaz, Verneuil and G. A. Terreil used a hydrogen-oxygen torch to fuse alumina powder with some added chromium salt. They obtained tiny particles, which Jannettaz identified as ruby. From this experiment, Verneuil began in earnest in 1888 to develop flame fusion growth of ruby.

Working with his student, Marc Paquier, Verneuil developed the flame fusion process well enough to write the details in a sealed report which he deposited at the Paris Academy of Science in 1891. After further improvement in decreasing growth stress, Verneuil deposited a second sealed document at the Academy of Science in 1892. Marc Paquier, presumably the same person who assisted Verneuil, displayed ruby crystals at the World Fair in Paris in 1900. The crystals, for which there was brisk demand, appear to have been made by the Verneuil process, not the Geneva process, and commercial production had already begun by 1900. In 1902, Verneuil announced that he had developed a flame fusion process for making ruby and he published full details in 1904.[7]

Figure 3 is taken from one of Verneuil's two U.S. patents. To make feed powder, ammonium aluminum sulfate and ammonium chromium sulfate were each recrystallized 4-5 times and a mixture of the two was calcined at 1000-1200°C to give a mixture of the oxides. Ground powder was placed in container B in Figure 3 and delivered into tube K by the tapping hammer D. Oxygen was also delivered through tube K and illuminating gas was delivered through tube S. The flame burned inside the ceramic muffle insulator M whose inside diameter was 25 mm and whose inside height was 105 mm. An alumina pedestal L held by a platinum tube could be lowered away from the flame by crank P as the crystal grew on the pedestal. A mica window covered by a steel shutter, neither of which is shown in Figure 3, enabled the operator to view the growing crystal inside the muffle.

The crystal growth process described in Verneuil's patent is shown in Figure 4. Powder falling through the flame was heated just below its melting point. The initial powder built up a conical pile in which the hot particles sintered together to make a rigid "sinter cone." The upper tip of the cone became molten when the cone got sharp enough. Fresh powder landing on the molten ball would melt and enlarge the crystal. Only the uppermost skin of the growing crystal was molten. As the crystal grew in a vertical direction, the pedestal was lowered to keep the top of the crystal at the correct location in the flame. Flame temperature during crystal growth was regulated by controlling the flow of oxygen. At the end of a growth run, the flame was shut and, if there was not too much strain, the crystal would not shatter. Even so, crystals had so much strain that a light tap at the end would split the crystal lengthwise into two halves. A typical growth time of 2 hours produced a 15 carat cylinder with a diameter of 6 mm and length of 25 mm.

In 1909 Verneuil was appointed chief chemist at the Paris laboratory of the New York jewelry company, L. Heller and Sons. His charge was to grow blue sapphire for jewelry. The origin of the blue color was not known until chemical analyses by Verneuil showed that natural blue sapphire always contained both iron and titanium. Armed with this knowledge, Verneuil was able to grow deliberately doped blue sapphire. The Paris laboratory was closed in 1911 with the successful completion of the project.

Ruby and sapphire manufacturing by the Verneuil process had begun in Europe prior to Verneuil's publication of 1904.[1] One of the largest Verneuil operations was that of Industrie de Piérres Scientifiques, Hrand Djévahirdjian in France and Switzerland. The company had a room with approximately 100 Verneuil torches operating around 1920. Heller Company had planned to manufacture blue sapphire in the U.S. but found that labor costs were too high to compete with European manufacturing. Blue sapphire was grown for Heller by Baikovsky Brothers in
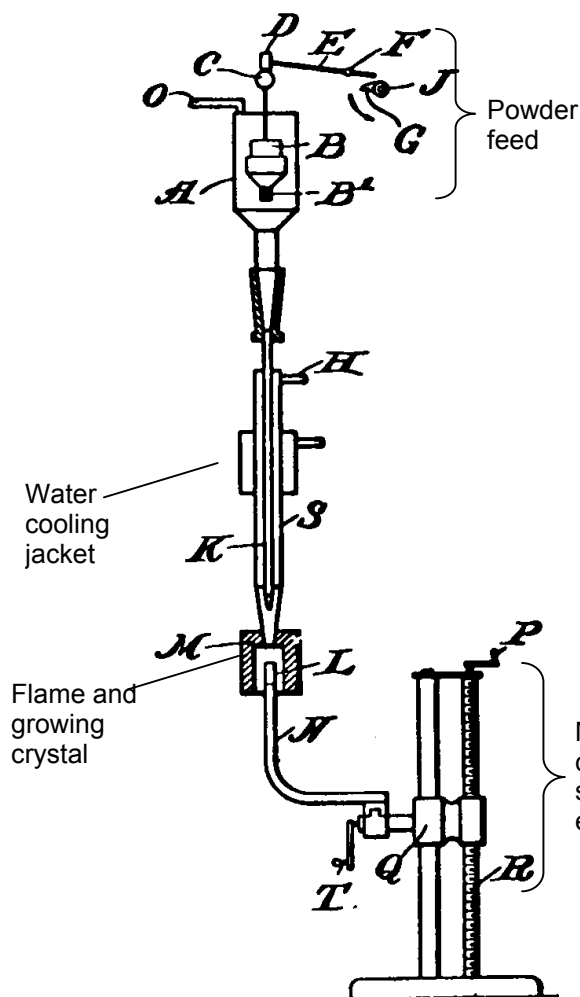
France.

Figure 3: Diagram of Verneuil's apparatus for growing sapphire. From U.S. Patent 1,004,505, September 26, 1911.

B. container of feed powder
D. hammer
G. rotating cam
O. oxygen feed tube
H. illuminating gas feed tube
K inner tube carries oxygen
S. outer tube carries illuminating gas
M. muffle (insulation) surrounding downward-pointing flame
L. ceramic pedestal
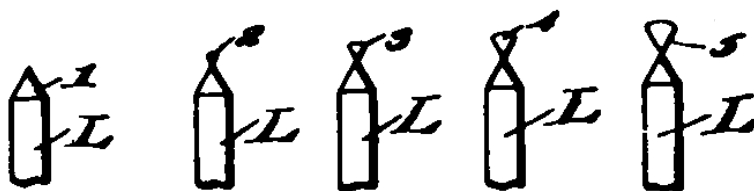P. crank for lowering pedestal to keep crystal at correct height in flame

Figure 4: Method of growing sapphire described in Verneuil's U.S. Patent 1,004,505.

Baikovsky had 3 torches in 1903, 80 in 1914, 400 in 1919, and 1600 torches in 1980. By 1980 there were approximately six large Verneuil manufacturers with a total capacity of 10^9 carats/yr. Most sapphire was cut into jewel bearings for watches and precision instruments. The process of cutting jewels wastes approximately 99% of the as-grown boule.

In the Soviet Union, S. K. Popov (1903-1953) began experiments with the Verneuil method in 1932.[4] By 1938 he had produced a semi-automatic growth apparatus which enabled the manufacturing of long thin rods suitable for making jewels for watches and instruments. From 1938 until his death, Popov worked at the Institute of Crystallography of the Academy of Sciences of the USSR. In 1945-50 he improved the equipment for making ruby rods, solving such problems as accurate supply of powder and uniform heating of the growing crystal. In 1951-53 he developed a new use for sapphire as a durable fiber guide in the textile industry. He also devised equipment for bending corundum rods into shapes. A commentary written by N. N. Sheftal' in 1959 stated that Popov's equipment was more advanced than that of Western Europe and that the crystal quality produced in the Soviet Union was higher than that available elsewhere.[4]

Birth of the Sapphire Industry in the United States

Prior to the publication by Verneuil in 1904, industrial production of ruby began in the town of Hoquiam, Washington in the period 1903-1904. The story pieced together by Nassau[1] states that two entrepreneurs, Polson and Ninemire, who had accumulated wealth in the lumber industry, hired an assistant of Verneuil to establish a flame fusion facility to grow ruby for jewelry. It was necessary to send boules to New York for cutting and the venture as a whole was not economical. The arrival of less expensive Verneuil ruby from Europe ended any hope of American production.

There was no further U.S. production of ruby or sapphire until America was cut off from European supplies of jewel bearings in World War II. The U.S. government issued development contracts which led to production by Linde Air Products Co. in Indiana in 1942. One advantage that Linde had for sapphire production was that Linde was a major supplier of industrial gases, including those used for the Verneuil torch. Linde was later acquired by Union Carbide Corp. After the war, the U.S., again, could not compete with Europe for economy in sapphire production. In the late 1940s Linde developed a process for making star sapphire and star ruby, which contain needles of titanium dioxide, for jewelry. Another market for sapphire was fiber guides in the textile industry. The Linde plant in Indiana was closed in 1974 and Union Carbide's Linde Crystal Products Division concentrated on Czochralski crystal growth in California and Washington State. In 1999 the Crystal Products Division was acquired by Bicron, a division of the French company, Saint-Gobain. In 2000 the division was renamed "Saint-Gobain Crystals and Detectors".

Czochralski Sapphire Crystal Growth

Verneuil's flame fusion process, perfected in 1892, hardly changed in the 70 years in which it was the only significant production method for sapphire. There is still significant demand for Verneuil material at the dawn of the 21st century because the method is the least expensive way to make sapphire and ruby whose quality is adequate for many applications. However, higher crystal quality demanded by electronic and optical applications, and the need for sizes and shapes that cannot be made by flame fusion, sparked the development of other ways to make sapphire after 1960.

The Czochralski crystal growth method was applied to sapphire in the early 1960s.[8] Then other growth methods were invented later in the 1960s. Edge-defined film-fed growth was developed in the U.S and the related Stepanov method was applied to sapphire in the U.S.S.R. The heat exchanger method was developed in the U.S. and gradient solidification was introduced in Israel.
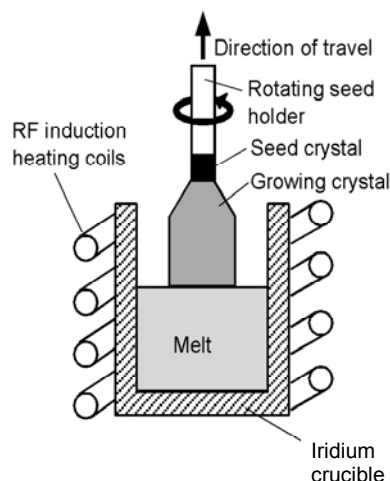

Figure 5: Czochralski crystal growth.

A resurgence of interest in ruby arose with the invention of the ruby laser in 1960 using a Verneuil boule grown by Union Carbide in 1959. It was quickly discovered that the optical quality of Verneuil boules was not adequate for lasers. This dilemma led to the development of sapphire growth by the Czochralski method at Union Carbide in the 1960s. In this process, alumina is melted in an iridium crucible in an atmosphere of 98% N_2 / 2% O_2. A seed crystal is then dipped into the liquid and withdrawn at a rate of 6-25 mm/h while rotating at a rate up to 30 rpm. As the seed is withdrawn, alumina from the melt crystallizes onto the seed. The diameter of the boule could be controlled by the rate of withdrawal of the seed. Boule diameters up to 11 cm could be obtained from a 15-cm-diameter crucible. Saint-Gobain in Washington State and Crystar Research (a division of Johnson Matthey) in Vancouver, Canada both produce sapphire today by the Czochralski method.

Edge-Defined Film-Fed Growth

Harold LaBelle, Jr. was a talented technician with only a high school diploma who joined Tyco Laboratories in Waltham, Massachusetts in 1962. Previously, he served as a Navy weather observer at White Sands Proving Ground and attended New Mexico State University. His early experience at Tyco was in the growth of semiconductor crystals by gradient freeze and "traveling solvent" methods, from which he gained an understanding of solid-liquid interface control. In 1965 he began work on an Air Force contract whose goal was to make sapphire fibers for reinforcement of metal matrix composites.[9,10,11] By analogy with silicon growth at other laboratories, LaBelle found that if he plunged a cold tungsten rod into molten alumina, small, crystalline alumina dendrites grew from the tungsten, which served as a seed. However, the longest dendrites were only 3 mm, which was much shorter than required. In an attempt to improve temperature stability, Labelle melted alumina in a tungsten boat in a vacuum evaporator. When a 0.25 mm tungsten wire was dipped into the melt and carefully lifted out, a sapphire crystal grew on the tungsten wire "seed". This process was essentially a Czochralski crystal growth that produced a carrot shaped sapphire crystal with the tapered tip attached to the last drop of molten alumina (Figure 6).

The final diameter of the sapphire depended on the diameter of the liquid drop remaining in Figure 6. LaBelle reasoned that a droplet of the right cross section would produce a filament of the desired cross section. A method was needed to feed liquid with a constant cross section from a reservoir so that long filaments could be produced. Therefore, Labelle floated a molybdenum washer on top of molten alumina and drew a fiber by Czochralski-like growth through the orifice of the washer (Figure 7). Several 1-mm-diameter crystals up to 30 cm long were grown in this manner. These results were impressive enough to secure additional funding for the project.
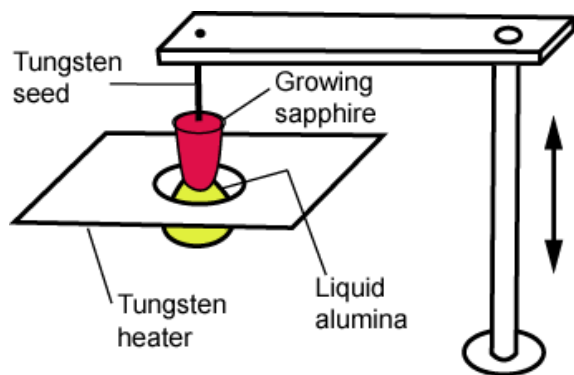
Figure 6. Czochralski-like growth of sapphire from molten alumina using tungsten wire as a "seed crystal". Redrawn from reference 10.
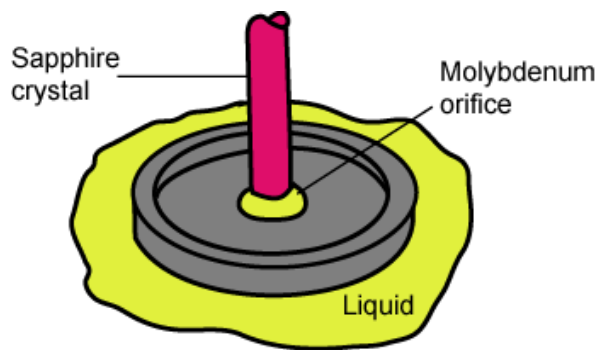

Figure 7. Sapphire crystal growth by the floating orifice technique. Redrawn from reference 10.

For several months, LaBelle grew crystals by this floating orifice technique. Eventually, he concluded that floating dense molybdenum on less dense alumina was too delicate for use in manufacturing. It then occurred to him that "a molybdenum capillary projecting out of the melt might yield the positive result that the floating orifice had, yet represent mechanical, and therefore, thermal stability as well."[10] The *self-filling tube* in Figure 8 provided filaments with more regular surfaces and 3-4 times as much strength as from filaments grown earlier.[10,12] The capillary in Figure 9, made from concentric molybdenum tubes, produced the first sapphire tubes. Many tubes and ribbons were grown from self-filling tubes in 1967.
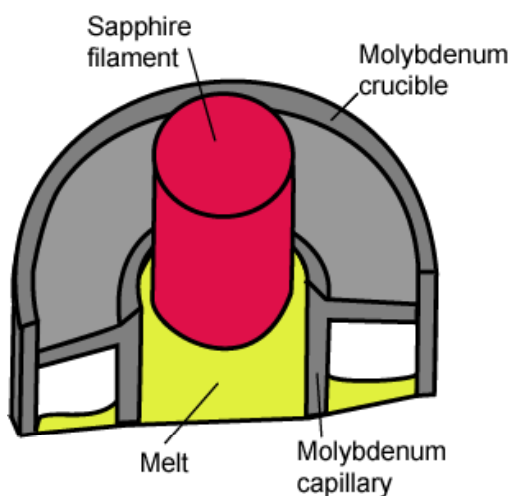
Figure 8. Self-filling capillary tube for filament growth. Redrawn from reference 13.
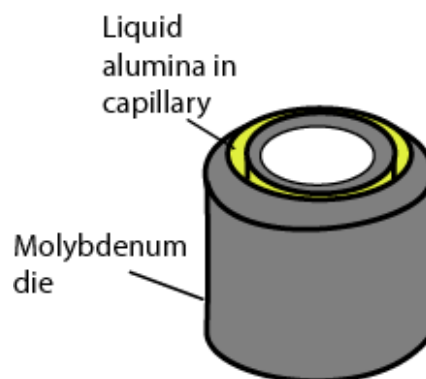
Figure 9. Self-filling capillary tube for tube growth. Redrawn from reference 10.

In a key observation, LaBelle noticed that sometimes the sapphire diameter grew larger than that of the orifice from which it was drawn. The difference depended on the angle of the upper surface of the orifice. If the top surface of the molybdenum were flat, the liquid would spread to the edge and then stop. A crystal grown from such a capillary would be just as wide as the outer diameter of the molybdenum. LaBelle and his assistant, John Bailey, built the die in Figure 10, which easily produced a tube whose outer diameter was equal to the outer diameter of the molybdenum. Because the dimensions of the sapphire tube grown in Figure 10 were controlled by the molybdenum die, Labelle's supervisor, Ed Mlavsky coined the term "edge-defined film-fed growth," or "EFG."
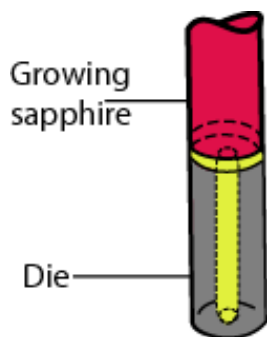
Figure 10. First edge-defined film-fed growth of a sapphire tube whose wall dimensions were equal to the dimensions of the molybdenum die. Redrawn from reference 10.
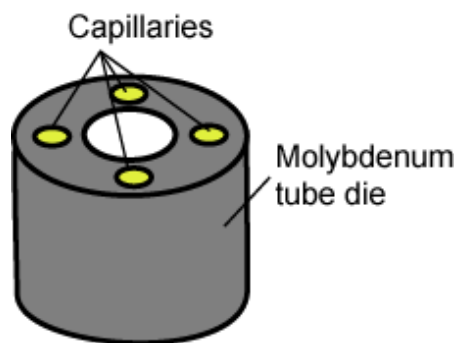
Figure 11. Die used to prove that the edges of the molybdenum die defined the edges of the sapphire crystal. Redrawn from reference 10.

To distinguish between edge-defined film-fed growth and self-filling tube growth, the die in Figure 11 was constructed. If the top surface of the molybdenum die controlled the shape of the crystal, then a uniform tube would grow from the molten alumina fed through the four capillary openings. Sure enough, the die produced a tube with uniform walls. "The uniqueness of EFG in shaping was therefore established ... since the capillaries were of totally different cross-sectional shape than the growing crystal."[10] LaBelle suggested calling the new process "continuous shaped film propagation," but Mlavsky's "edge-defined film-fed growth" prevailed.

The purpose of the Air Force contract at Tyco Laboratories was to grow long filaments of sapphire. To accomplish this, LaBelle had to invent clever mechanisms to guide the growing fiber and to pull long lengths with a small machine. Fibers grown in the Air Force program in 1965-66 were nearly opaque and there was no immediate demand for the product. However, in the 1970s, transparent material could be grown in many shapes.[11,12,13] An application with a significant market was $12.5 \times 12.5 \times 0.6$ mm windows for erasable programmable read-only memory chips. EFG growth of transparent sapphire optical fibers for high temperature environments was stimulated in the 1980s by funding from the Department of Energy.

Concurrent with the work of LaBelle in the 1960s, Stepanov independently applied his shaped growth method to sapphire in the Soviet Union.[14,15] His method was originally used in the late 1930s to grow shaped metal crystals.[16] The Stepanov method uses wettable or nonwettable aids to shape the melt column which, in turn, dictates the shape of the grown crystal (Figure 12).[13] By contrast, in edge-defined film-fed growth, the shape of the die, not the shape of the melt column, controls the shape of the crystal.

In 1970 Tyco created the Saphikon Division to produce EFG sapphire in Waltham. In 1978 the Saphikon Division moved to Milford, New Hampshire. In the 1970s and 1980s Saphikon received the bulk of its revenue by licensing the EFG process to companies such as Kyocera, RCA, Corning, and Allied Signal, all of whom saw commercial potential for sapphire substrates for the newly developing silicon-on-sapphire electronics technology.   In 1982, Joseph Gaziano, the president of Tyco, died. The new president, John Fort, sought to sell the Saphikon Division, which had less than two million dollars

Figure 12. Wettable shaping aid used in Stepanov growth. The dimensions of the crystal are determined by the dimensions of the liquid feed column. Redrawn from reference 13.

per year in revenue. Eventually he made a deal with LaBelle that was "too good to refuse". LaBelle purchased Saphikon in 1985 and resold it at a profit in 1987. Saphikon remained independent until 2000 when Saint-Gobain purchased the company and the rights to make sheets, rods, tubes, and 3-dimensional shapes. The newly formed, independent company Photran retained exclusive rights to manufacture sapphire fibers.

Kyocera in Japan acquired EFG technology from Saphikon and further developed the process. Kyocera sells *r*-, *a*-, or *c*-plane sheets up to 20 cm wide x 30 cm long x 0.02-2 cm thick. Kyocera also sells *c*-axis rods and tubes.

Heat Exchanger Method

The Heat Exchanger Method (HEM) for growing large sapphire boules was invented by Fred Schmid and Dennis Viechnicki at the Army Materials Research Lab in Watertown, Massachusetts in 1967.[17,18] Fresh out of college in the early 1960s, Schmid worked in manufacturing at the Watertown Arsenal, where he gained experience in the directional solidification of metals and with a helium-cooled arc furnace for casting titanium. He then went to Northeastern University to earn a masters degree in materials science. Returning to the Watertown Lab in 1967, Schmid set to work with Viechnicki on directional solidification of an alumina melt onto a sapphire seed crystal.

The modern implementation of Schmid and Viechnicki's heat-exchanger method at Crystal Systems in Salem, Massachusetts is shown in Figure 13. A sapphire seed crystal is placed at the bottom of a molybdenum crucible which is then loaded with pure alumina crackle, a byproduct of the Verneuil process. The furnace is evacuated and resistively heated to melt the crackle while keeping the seed just below its melting point by passing helium gas through the heat exchanger beneath the center of the crucible. Heat and vacuum help purify the alumina by vaporizing some impurities. After partial melting of the seed, helium flow is increased to cool the seed and initiate crystallization of alumina onto the seed. The furnace is held at constant temperature during growth of the crystal, which proceeds out from the seed in 3 dimensions. After crystallization is complete, the furnace temperature and the helium flow are decreased and the boule is slowly annealing *in situ*. The long slow cooldown produces sapphire of the highest crystal quality. Boules with a diameter of 34 cm and a mass of 65 kg are routinely produced and boules up to 38 cm have been grown.

Single crystals of sapphire were grown in an 18-mm-diameter crucible in 1967 at Watertown. By 1969, after about 50 attempts, crack-free sapphire with a diameter of 76 mm was grown. By 1971 the diameter was up to 152 mm. The first patent for the process, which was then known as the Schmid-Viechnicki technique, was issued in 1969.
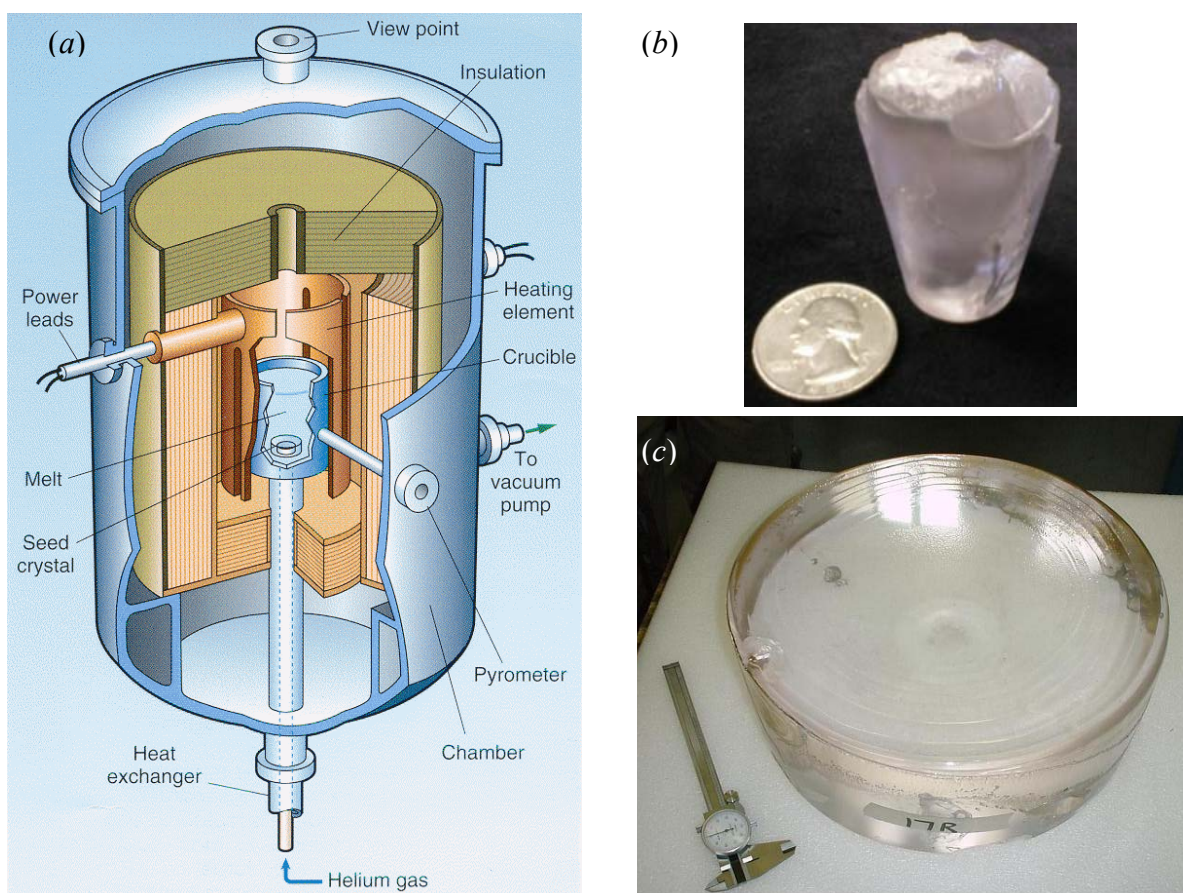
Figure 13: (*a*) Furnace used at Crystal Systems to grow sapphire by the Heat Exchanger Method. (*b*) The first sapphire boule grown at Watertown in 1967. (*c*) Production-quality 34-cm-diameter sapphire boule. Courtesy Crystal Systems, Inc.

By early 1971, Schmid was convinced that the new method was a breakthrough and wanted to find a commercial market for the product. He found interest at Inselec and Insaco in obtaining sapphire wafers for silicon-on-sapphire electronics. Schmid persuaded a sailing buddy and an accountant to invest in creating the company, Crystal Systems, of which Schmid would own 51%. The company was incorporated in August 1971 after Schmid had purchased a scrapped furnace from Raytheon in July. He began refurbishing the furnace in his garage and soon moved the operation to Shetland Industrial Park in Salem. For the first year of the company, Schmid held his old job at Watertown and worked on the furnace at night. By July 1972 he grew his first 152-mm-diameter boule, from which 51-mm cores were drilled for silicon-on-sapphire substrate wafers. In. September 1972 Schmid resigned from Watertown to devote full attention to Crystal Systems. He hired his first helper (who was "just getting out of high school") and his wife handled advertising. First-year sales were less than fifty thousand dollars. Shortly after the first advertising went out in 1974, Schmid received a letter from Union Carbide indicating that Crystal Systems was infringing on their patent and offering to license Union Carbide technology. This claim led Schmid to clarify the difference between the processes and to obtain a patent for his technique, whose name he changed to "heat-exchanger method" because of its unique, controllable heat exchanger.

In the mid 1970s Crystal Systems began to hire full-time employees. Schmid developed a fixed-abrasive slicing technique using a diamond-impregnated blade or wire to slice wafers from a cylinder with minimal loss of material. The National Aeronautics and Space Administration selected HEM sapphire for use in satellites because of its extremely low optical scatter. In 1978 the company moved to its current, larger quarters in the same industrial park. In 1979 Crystal Systems received a contract to grow laser-quality ruby in one of the first actions of the government's new Small Business Innovative Research program. In 1987-89, titanium-doped sapphire for lasers was commercialized. Military and commercial markets for sapphire expanded greatly in the 1980s. In 1974 Crystal Systems got its first government contract to grow silicon and in 1977 Chandra Khattak at Crystal Systems used the heat-exchanger method to grow crack-free polycrystalline silicon ingots in high purity silica crucibles for the first time. HEM silicon for photovoltaics and equipment for growing silicon are currently major products of Crystal Systems, in addition to sapphire and crystal slicing equipment. HEM silicon ingots weighing 240 kg with a cross section of 69×69 cm are routinely produced.

Sapphire Domes

One of the most demanding applications for an infrared window material is the seeker dome on an infrared-guided missile. The dome must withstand stress from very rapid heating and it must survive collisions with raindrops, sand particles, and insects in the air. Among the infrared-transparent materials available in the 1980s, sapphire was clearly the most durable with respect to thermal stress and particle impact. However, the cost of growing sapphire was high and the cost of fabricating it into an optically polished hemisphere was even higher. To decrease the cost, the government invested in two efforts to grow near-net-shape domes which would require relatively little machining after growth.

One Navy-funded effort at Saphikon led to a Manufacturing Technology contract in 1989-92. A curved sapphire seed crystal was placed in contact with a curved slit at the top of a molybdenum die for EFG growth. The seed was slowly withdrawn in a path that traced an arc in space. The result was an as-grown dome, such as that in Figure 14, which could be ground and polished into a finished dome. However, the crystal quality was not as high as desired and the manufacturing process was never optimized.[19,20]

Figure 14: As-grown EFG sapphire produced by Saphikon.[19,20]

Another Navy Small Business Innovative Research contract was conducted at Crystal Systems. Work done in the mid to late 1980s used the apparatus shown at the left in Figure 15 to grow the near-net-shape domes at the right.[21,22,23] Two hemispheric molybdenum mandrels were inserted into the crucible in which sapphire was grown. After a boule was grown and cracked apart, sapphire that crystallized in the volume between the two mandrels had a hemispheric shape. This method suffered from cracks extending into the boule and it was never taken beyond an initial demonstration.
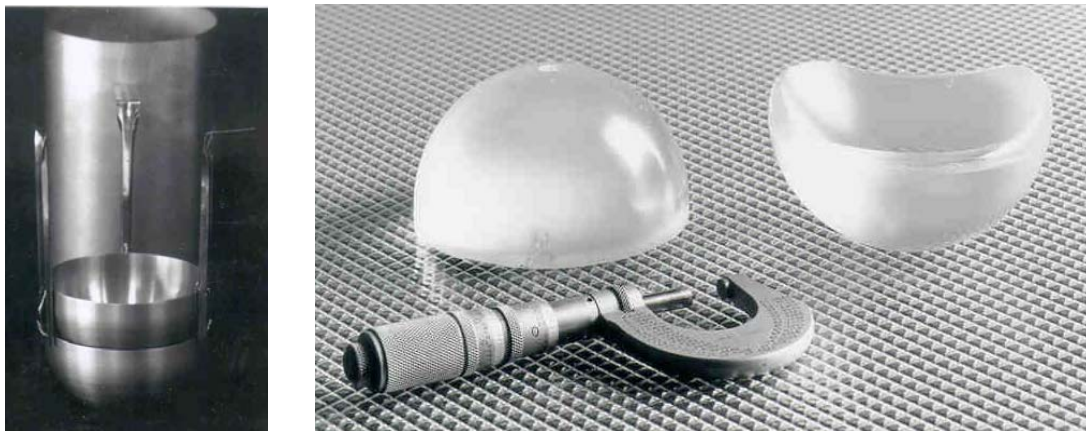
Figure 15: Molybdenum apparatus at left was used at Crystal Systems to grow near-net-shape sapphire domes at right.[21-23] Photos courtesy Crystal Systems.

Domes were formerly produced from sapphire boules by machining each dome out of a cylindrical piece of material, as shown at the left in Figure 16. This process wastes valuable material and requires a great deal of machining. A cost effective method for making domes—the process used today in the U.S.—is called *scooping*. Shown at the middle of Figure 16, 7 nested domes could be taken from the same volume of material that produced 3 domes by conventional machining. Diamond-impregnated cutting tools shown at the right of Figure 16 are used to cut out first the inner surface and then the outer surface of consecutive domes. In the cutting process, the sapphire is rotated in one direction while the tool is rotated against it in the opposite

direction. At the end of the scooping, neighboring domes are connected by a small cylinder of material at the apex. The domes are broken apart by tapping and then they are ground and polished to their final finish.
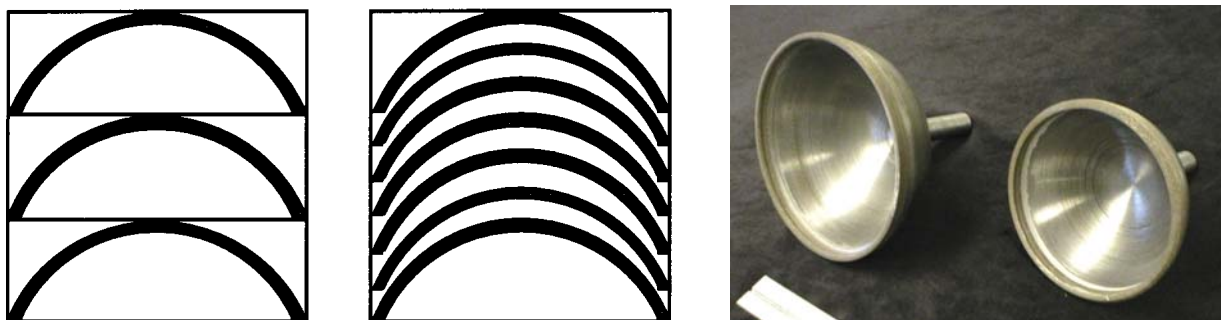
Figure 16: Line drawings compare conventional use of a boule to make 3 domes and scooping to make 7 domes from the same volume. Photograph shows diamond-impregnated scooping tools used at Crystal Systems for scooping sapphire. Photo courtesy Crystal Systems.

Rotem Industries, which was founded in 1969, provides sapphire products for defense applications. The gradient solidification method for sapphire growth was developed at Rotem to produce high quality, near-net-shape domes.[24,25,26,27,28] In Figure 17, alumina is loaded into a hemispheric molybdenum crucible containing a sapphire seed at the bottom. The crucible is heated in vacuum to produce a gradient of temperature, with the highest temperature at the top. When the seed has partially melted, the temperature is lowered in a carefully controlled manner so that crystallization proceeds out from the seed crystal. An as-grown hemispheric dome and a solid hemisphere are shown in Figure 18.

Figure 17: Apparatus for growing sapphire by gradient solidification at Rotem Industries in Israel.

14
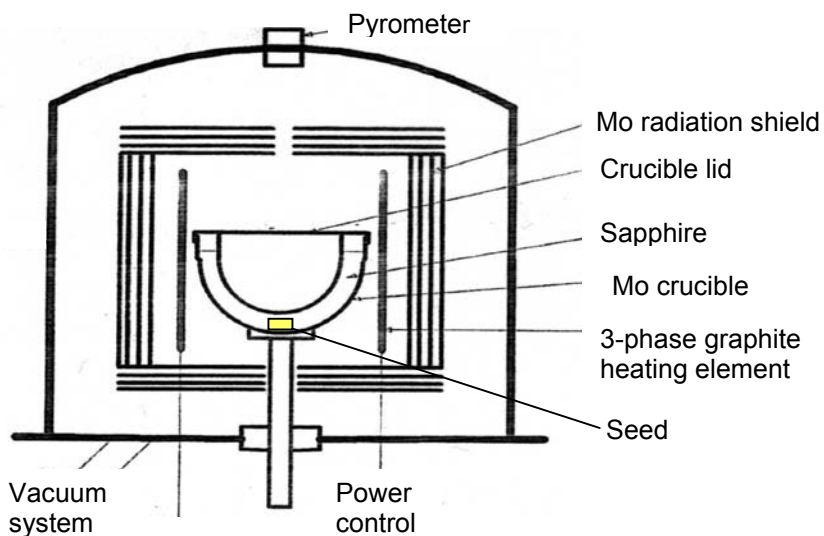
In the heat-exchanger method, highest crystal quality is produced when growth takes place along the *a*-axis of the crystal. For the boule in Figure 13(*c*), the *a*-axis is the cylindrical axis. The optical axis of sapphire (the *c*-axis) is perpendicular to *a* and comes out the curved side of the boule. To make *c*-axis domes, a cylindrical core is drilled from the side of the boule and domes are scooped out from the core. In Rotem's gradient solidification method, the thermal mass is low enough to permit the growth of good quality *c*-axis boules and domes, as well as *a*-axis material.

Polished   As-grown dome   As-grown boule

Dome viewed through crossed polarizers
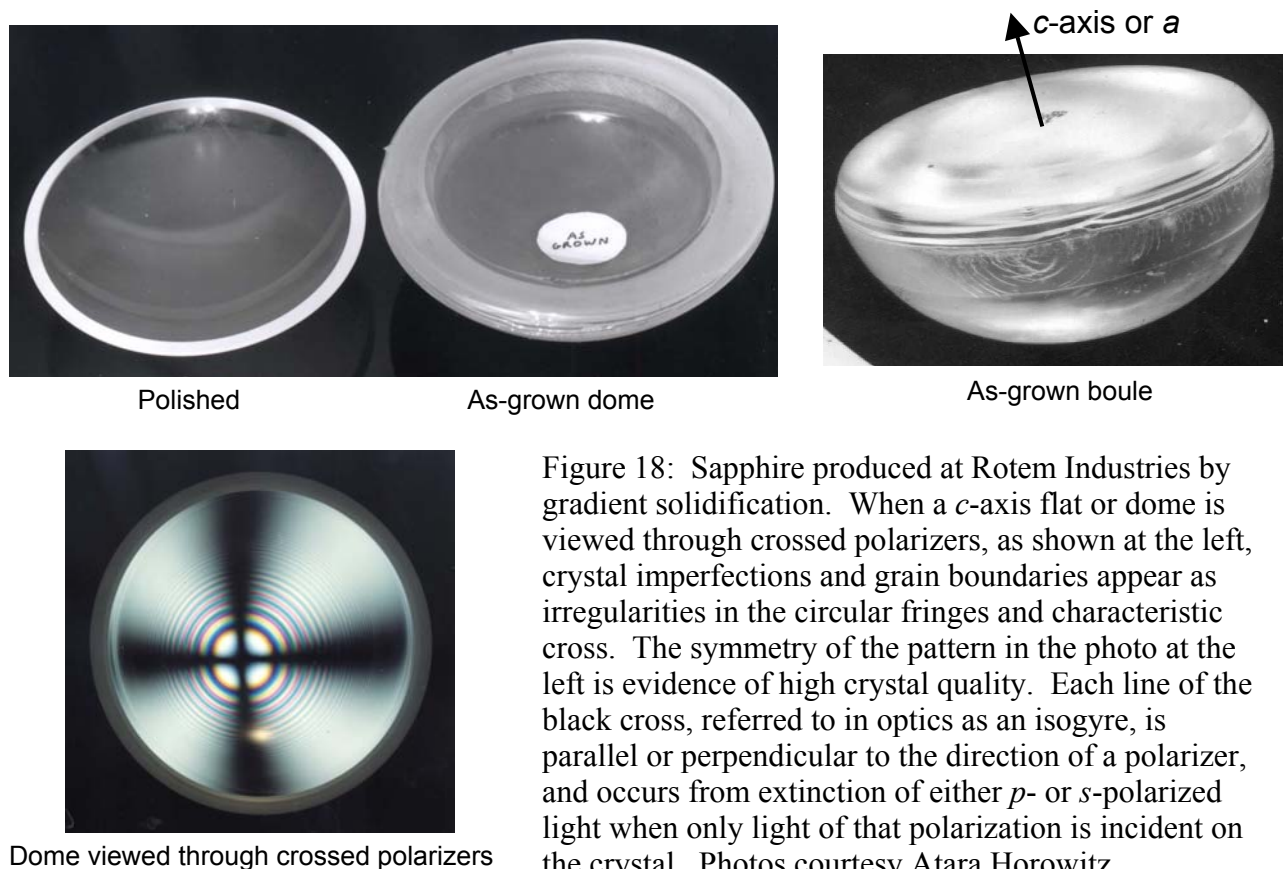
Figure 18: Sapphire produced at Rotem Industries by gradient solidification. When a *c*-axis flat or dome is viewed through crossed polarizers, as shown at the left, crystal imperfections and grain boundaries appear as irregularities in the circular fringes and characteristic cross. The symmetry of the pattern in the photo at the left is evidence of high crystal quality. Each line of the black cross, referred to in optics as an isogyre, is parallel or perpendicular to the direction of a polarizer, and occurs from extinction of either *p*- or *s*-polarized light when only light of that polarization is incident on the crystal. Photos courtesy Atara Horowitz.

Outlook

Current issues for sapphire production for windows and domes include: (1) The cost of sapphire is high. Much of the cost is in machining and polishing. (2) There is a need for larger area windows. The EFG method can make inherently large windows. The Heat Exchanger method has been scaled up to 38-cm-diameter, but larger sizes would be desirable. Materials Systems, Inc. has demonstrated a way to bond sapphire panes to each other to make large windows, but the bond lines are not as strong as sapphire and they provide an optical discontinuity.[29] (3) Optical fabrication is not well enough controlled to give reproducible mechanical properties. It is virtually impossible to know the mechanical strength of a particular sapphire part unless it is proof tested. In the absence of proof testing, designs must be conservative to be reliable.

Acknowledgements

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Soviet
Verneuil
Ruby
Circa 1950
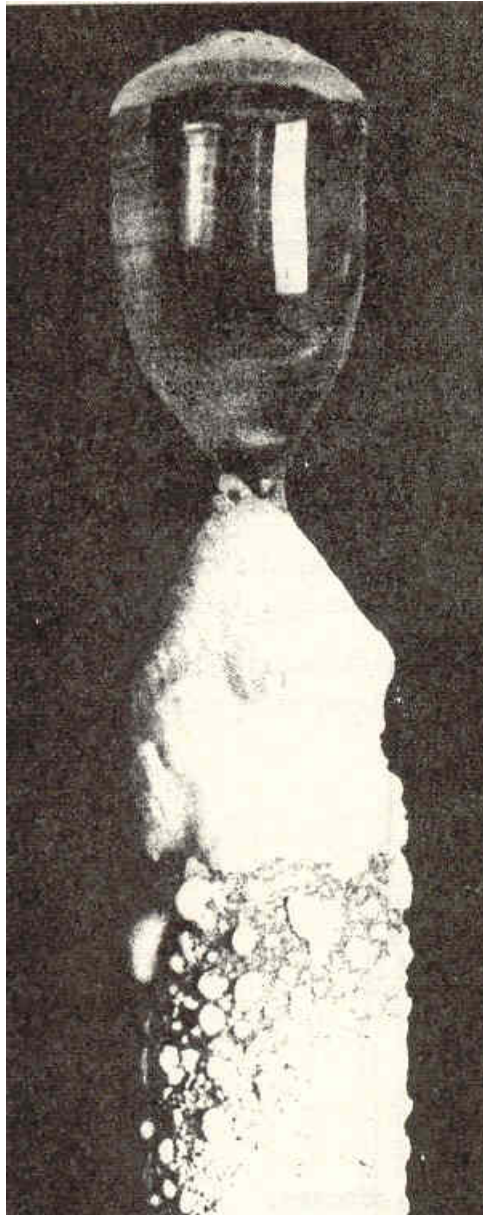
A Century of Sapphire Crystal Growth

Dan Harris
Naval Air Systems Command
China Lake, California
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May 2004

Home

Agenda

Sapphire, also called corundum, is Al_2O_3

Pure Al_2O_3 is colorless, but…

Ruby red color comes from several percent Cr^{3+} substituted for Al^{3+}

Blue sapphire color comes from a combination of Fe^{2+} + Ti^{4+} impurities

Fe^{3+} + Ti^{3+}
_____

Charge-transfer absorption band

$\lambda_{max} \approx 600$ nm

Fe^{2+} + Ti^{4+}
_____
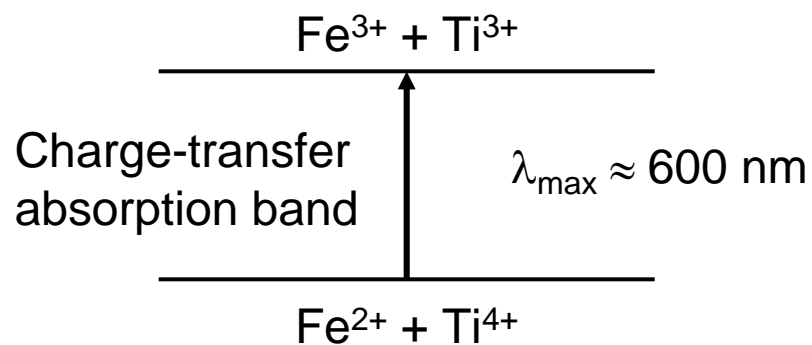
Sapphire Crystal
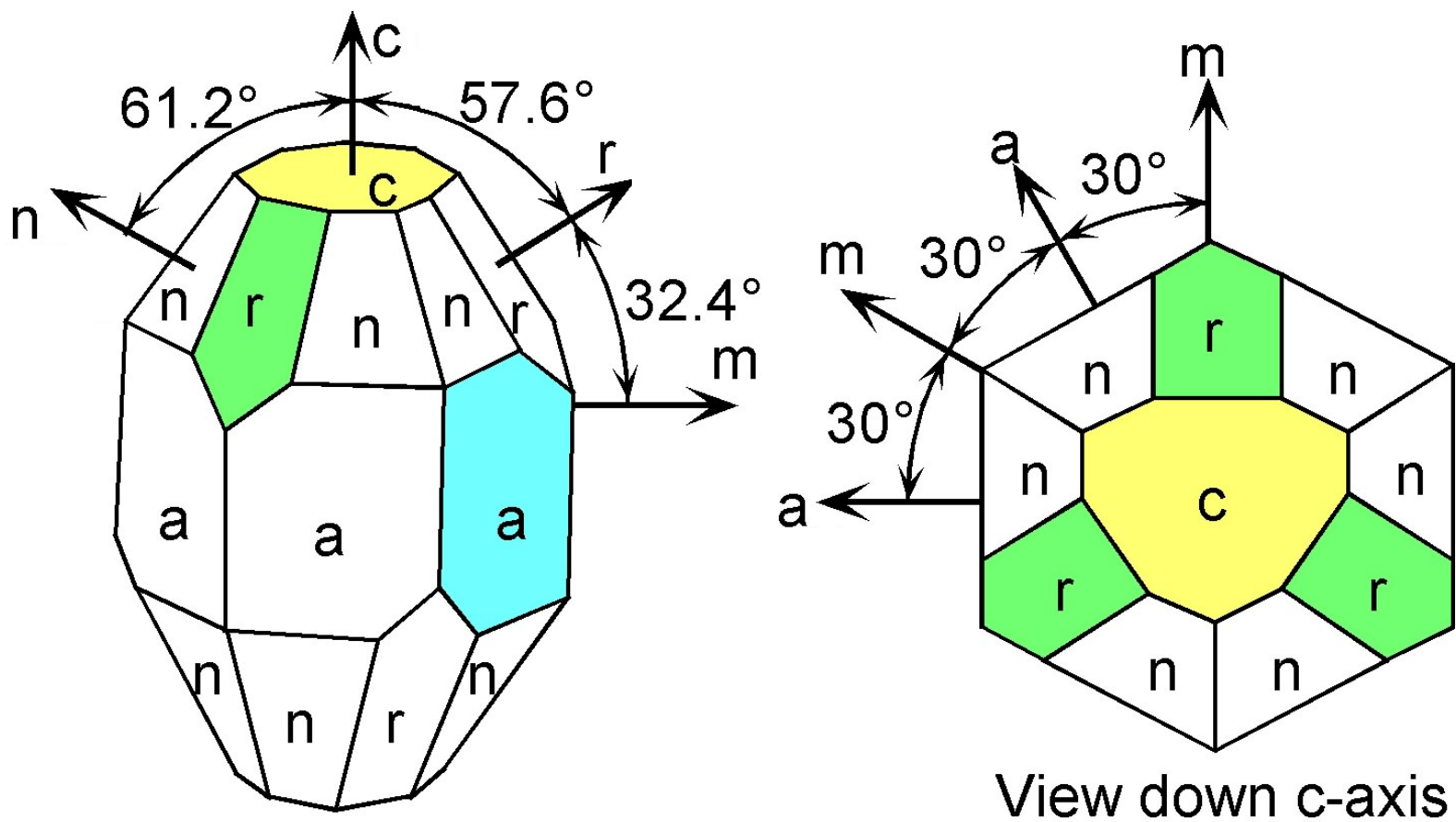
Melting point = 2050°C

Mohs hardness = 9

History of artificial ruby and sapphire:
Kurt Nassau, "Gems Made by Man" (Chilton Book Co., 1980)

- 1800: Ruby and sapphire were thought to consist of Al_2O_3 and SiO_2

- 1817: Gay-Lussac:

$$(NH_4)Al(SO_4)_2 \cdot 12H_2O \xrightarrow{\text{Heat}} \text{pure } Al_2O_3$$
Ammonium alum

Joseph Louis Gay-Lussac
1778-1850
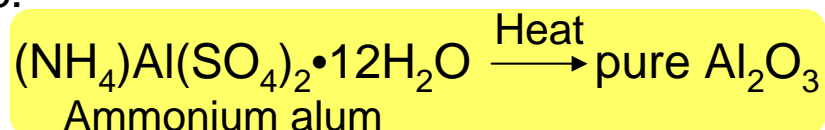
- 1840: Rose: Found SiO_2 in sapphire is from agate mortar used for grinding

- 1837-72: Gaudin: Fused alum + Cr salt with torch → hard red particles

- 1800s: Other corundum reports: Senarmont, Ebelman, Moissan, Parmantier, Boettger, Bruhns, Brun, Debray, Deville, Caron, Daubré, Doelter, Elsner, Friedel, Grandeau, Hautefeuille, Houdard, Loyer, Mallet, Medanich, Meunier, Morozewicz, Oetling, Perrey, Schuch and Weinschenk

- 1877: Edmund Frémy (1814-1894), Museum of Natural History, Paris
  Lead oxide → lead aluminate
  Lead aluminate + silica → lead silicate + thin, fragile corundum crystals
  Addition of 2% $K_2Cr_2O_7$ to reaction → ruby crystals

Auguste V. L. Verneuil, age 19
(1856-1913)

At age 17, Verneuil applied to work with Frémy at the Museum of Natural History, Paris. Verneuil was hired to work on flux growth of ruby.

Verneuil earned bachelors, masters, and Ph.D while working for Frémy.

1892-1905: Professor of Applied Chemistry at Museum of Natural History. Interests:

- chemistry of selenium
- phosphorescence of zinc blende
- rare earth elements
- purification of glycerin
- high-refractive-index glass for telescopes
- growth of ruby and sapphire

1876-1892: Frémy and Verneuil - Flux Growth of Ruby
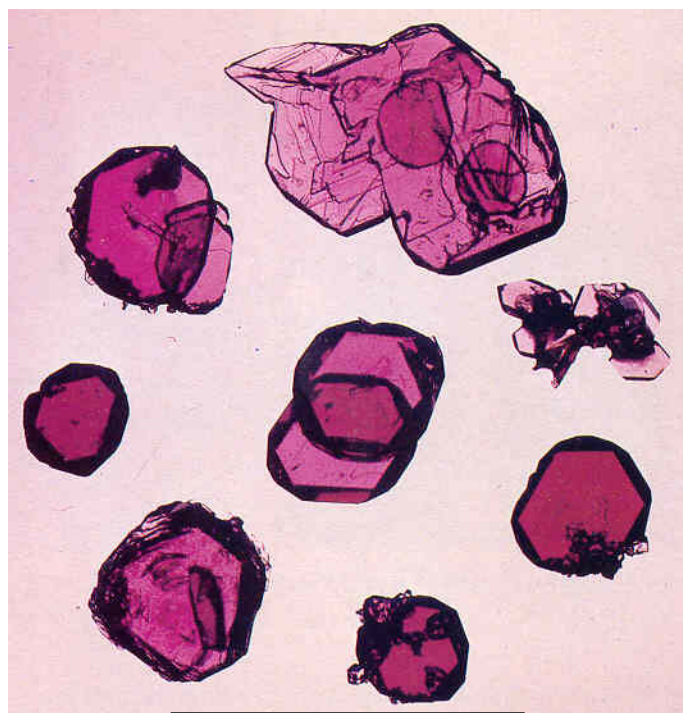
10 mm

Crystals up to 1/3 carat
(1 carat = 200 mg)

Crystallization of Al_2O_3 + $K_2Cr_2O_7$ from flux of KOH and BaF_2 at 1500°C in porous 800-mL crucible

$$3BaF_2 + Al_2O_3 \rightarrow 2AlF_3(g) + 3BaO \qquad (1)$$

$$2AlF_3(g) + 3H_2O \rightarrow Al_2O_3 + 6HF \qquad (2)$$

$$2HF + BaO \rightarrow 3BaF_2 + H_2O \qquad (3)$$
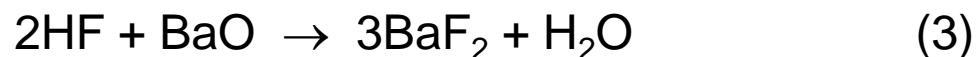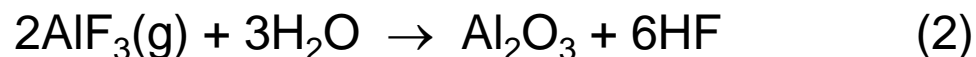
In attempts to increase crystal size, work was transferred to large ovens of Saint-Gobain and Appert glass factories with 50-L crucibles

Vapor phase nucleation in reaction (2) occurs in many small cavities and prevents growth of large crystals

1891: Frémy publishes book summarizing flux growth of ruby

Frémy retired in 1892 and died in 1894

Frémy and Verneuil Flux Growth
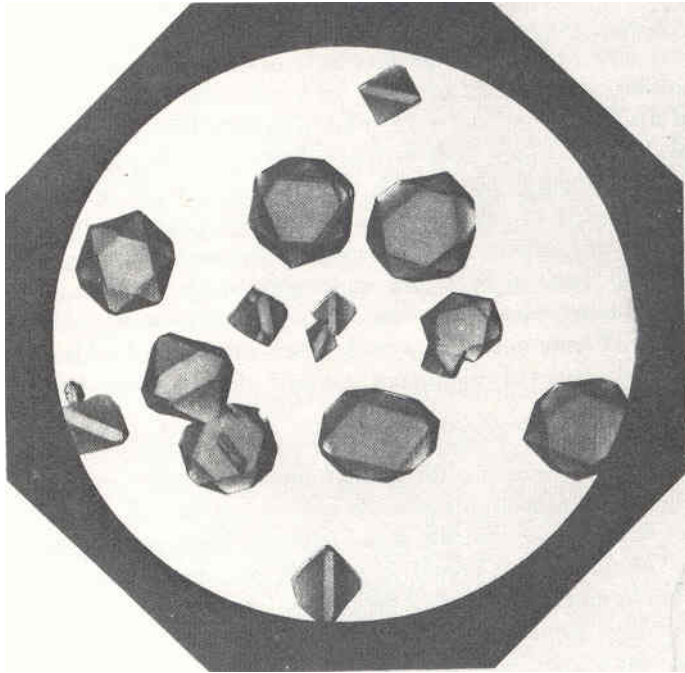
Flux-grown ruby
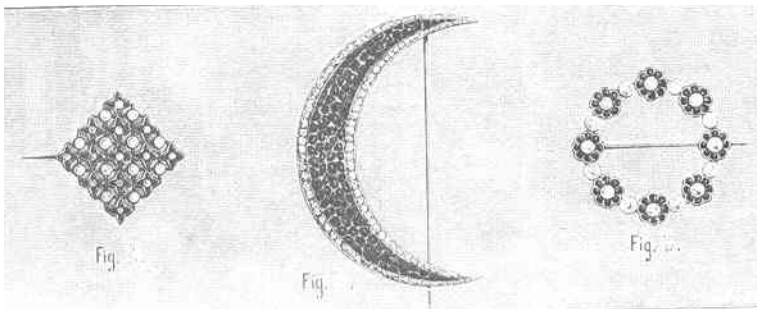
Jewelry with synthetic ruby
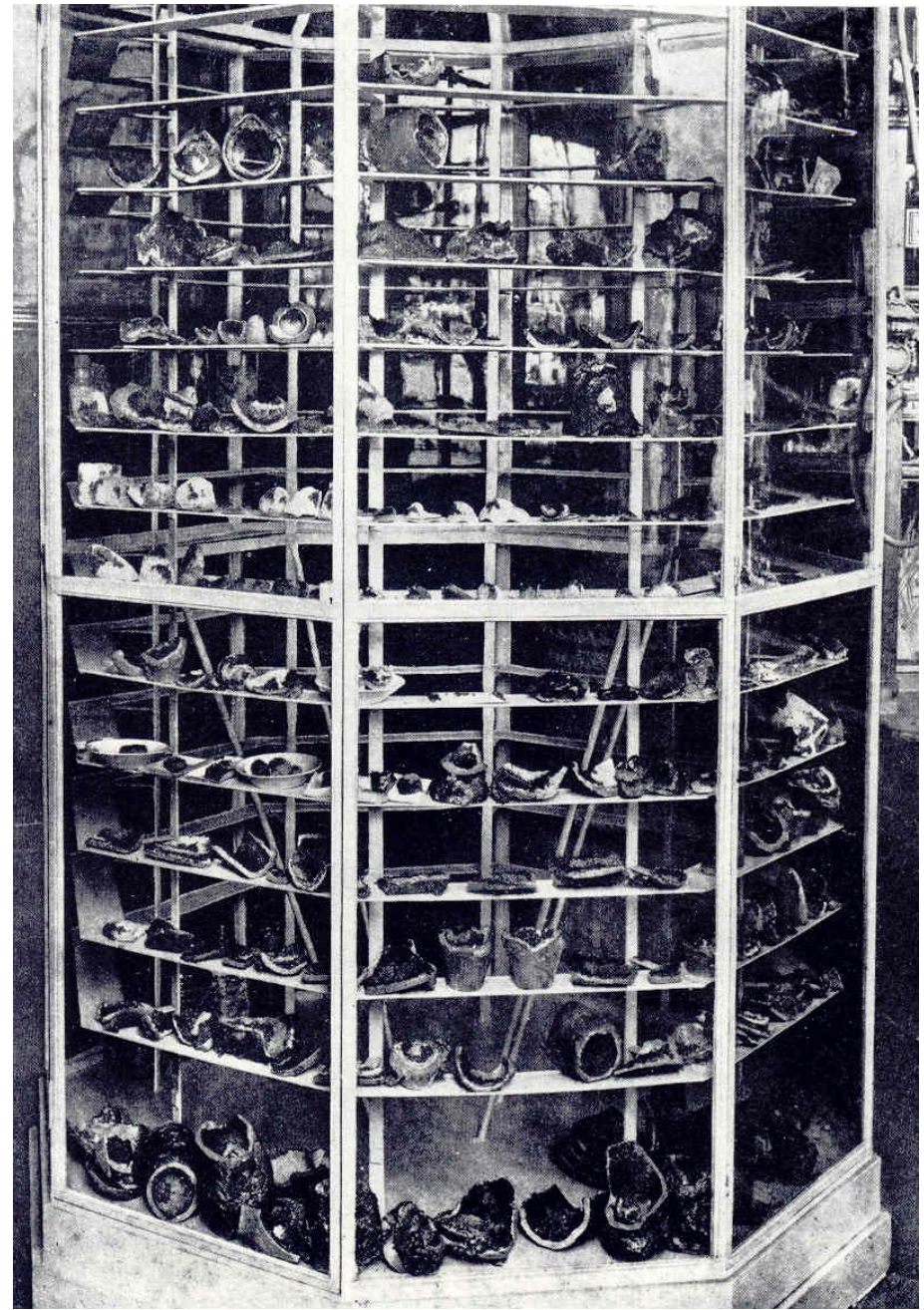
Frémy's storage cabinet (1891)

Geneva Ruby
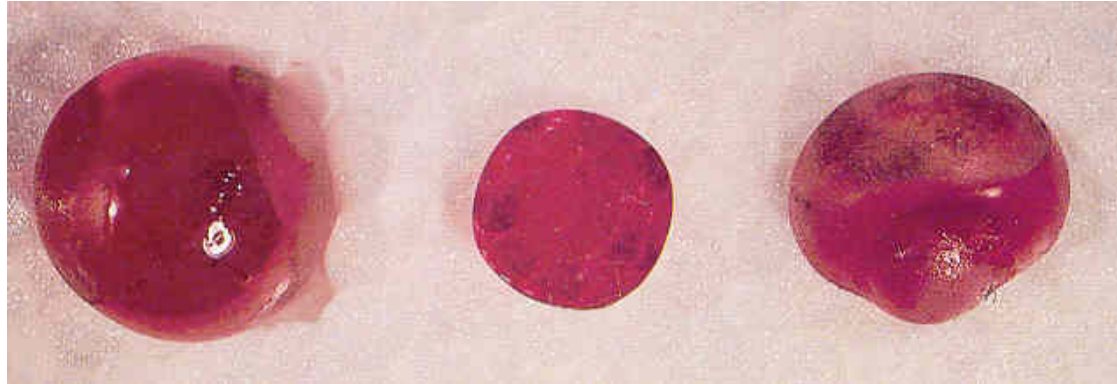
- 1885: Rubies of quality worth $1000-$2500/carat appeared on market from Geneva

- 1886: Prof. F. Friedel of Sorbonne observed gas bubbles in Geneva ruby and concluded that stone was made by high-temperature fusion process

- 1886: French Syndicate of Diamonds and Precious Stones rules Geneva ruby is man-made and must be sold as "artificial" $\Rightarrow$ price drops to $25-$40/carat

- 1886: G. F. Kunz of Tiffany examined Geneva ruby and concluded (probably incorrectly) that it was made by Frémy/Verneuil flux growth process

- 1904: Geneva ruby production ceases when Verneuil published his process

Geneva Ruby Growth Process as Reconstructed by Kurt Nassau
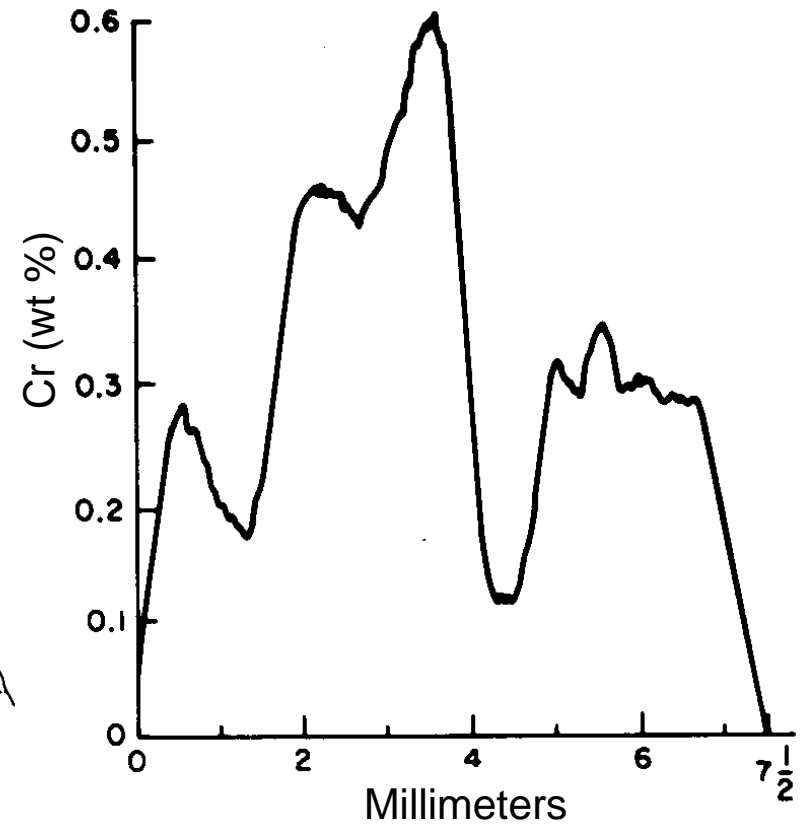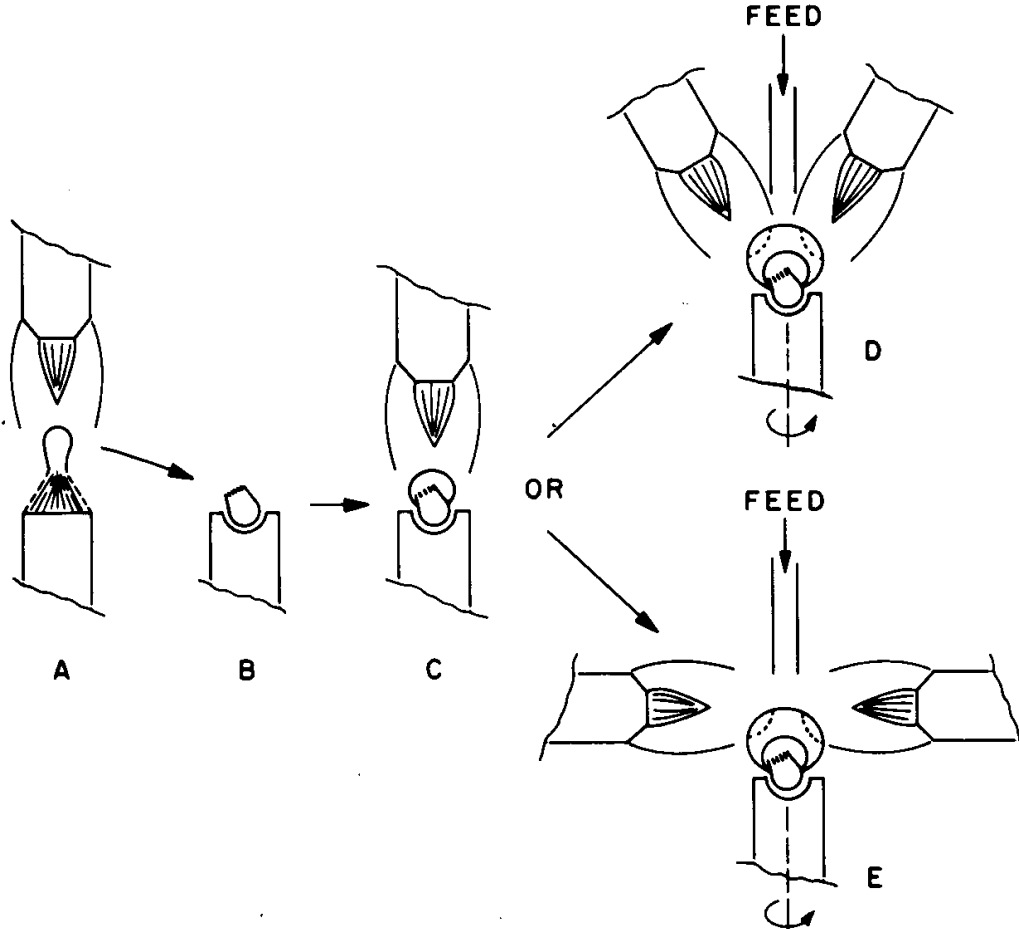
A. Tiny boule grown at tip of sinter cone from pure Al_2O_3 powder + Cr salt
B. Break off and turn boule over
C. Further growth
D. Complete growth with 2 torches and rotation of boule support

Discontinuities in Cr content of Geneva ruby correspond to different stages of growth process

Origins of Flame Fusion (Verneuil) Crystal Growth

- 1886: Mineralogist P. M. E. Jannettaz at Museum of Natural History, Paris, examined Geneva ruby and concluded that fusion was involved in its fabrication. Jannettaz discussed his observations with Verneuil.

- 1886: Verneuil and G. A. Terreil fused alumina powder plus Cr salt to produce microscopic single-crystal ruby, as confirmed by Jannettaz.

- 1888: Verneuil begins to investigate solidification of molten Al_2O_3 as an alternative to flux growth. The only practical way to obtain 2050°C needed to melt Al_2O_3 was H_2-O_2 torch or gas-O_2 blow torch.

- 1891: Working with his student, M. Pacquier, Verneuil had developed most of what we now call Verneuil flame-fusion crystal growth. Verneuil deposited details of the process in a sealed document at the Paris Academy of Science. Crystal cracking was main unsolved problem.

Initial fused region where tiny crystal begins to grow
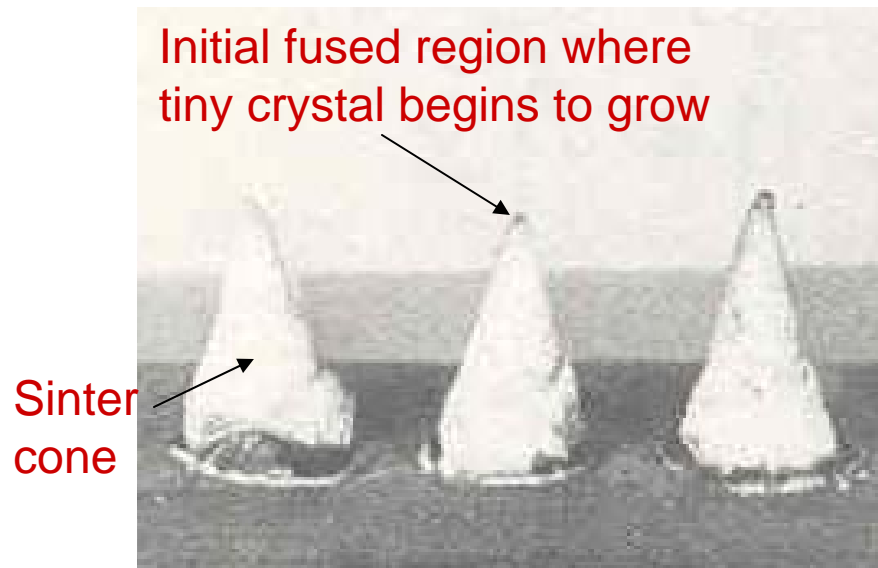
Sinter cone

Initial stages of Verneuil-grown ruby in Museum of Arts and Sciences, Paris

- 1892: Verneuil eliminated crystal cracking by making contact area between ruby crystal and sinter cone as small as possible. A second sealed document with details was deposited at Paris Academy of Science.

- 1900: Pacquier exhibits ruby crystals at Paris World's Fair. Source of rubies was unknown, but it was reported that the Paris manufacturer made ruby by the new Verneuil process (not the Geneva process) and "was able to sell all of his production to France and Germany."

- 1902: Verneuil announces details of flame fusion process

- 1904: Full publication: A. Verneuil, "Memoire sur la reproduction du rubis par fusion," *Annales de Chimie et de Physique* Ser. 8, 3: 20-48 (1904)

Verneuil's Flame Fusion Apparatus

Powder feed

Torch pointing down

Muffle furnace crystal growth zone

Mechanism to lower crystal during growth

Nassau, *Gems Made by Man*
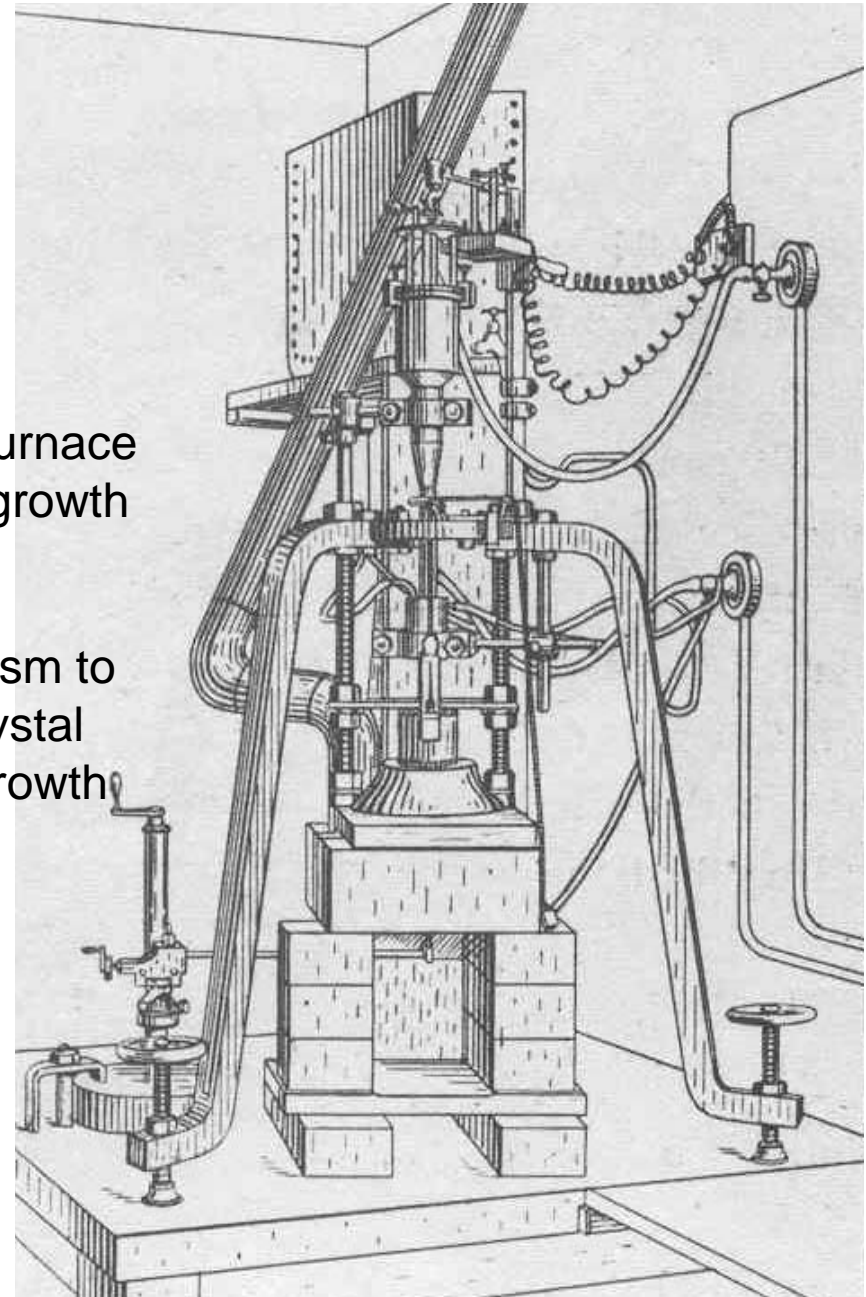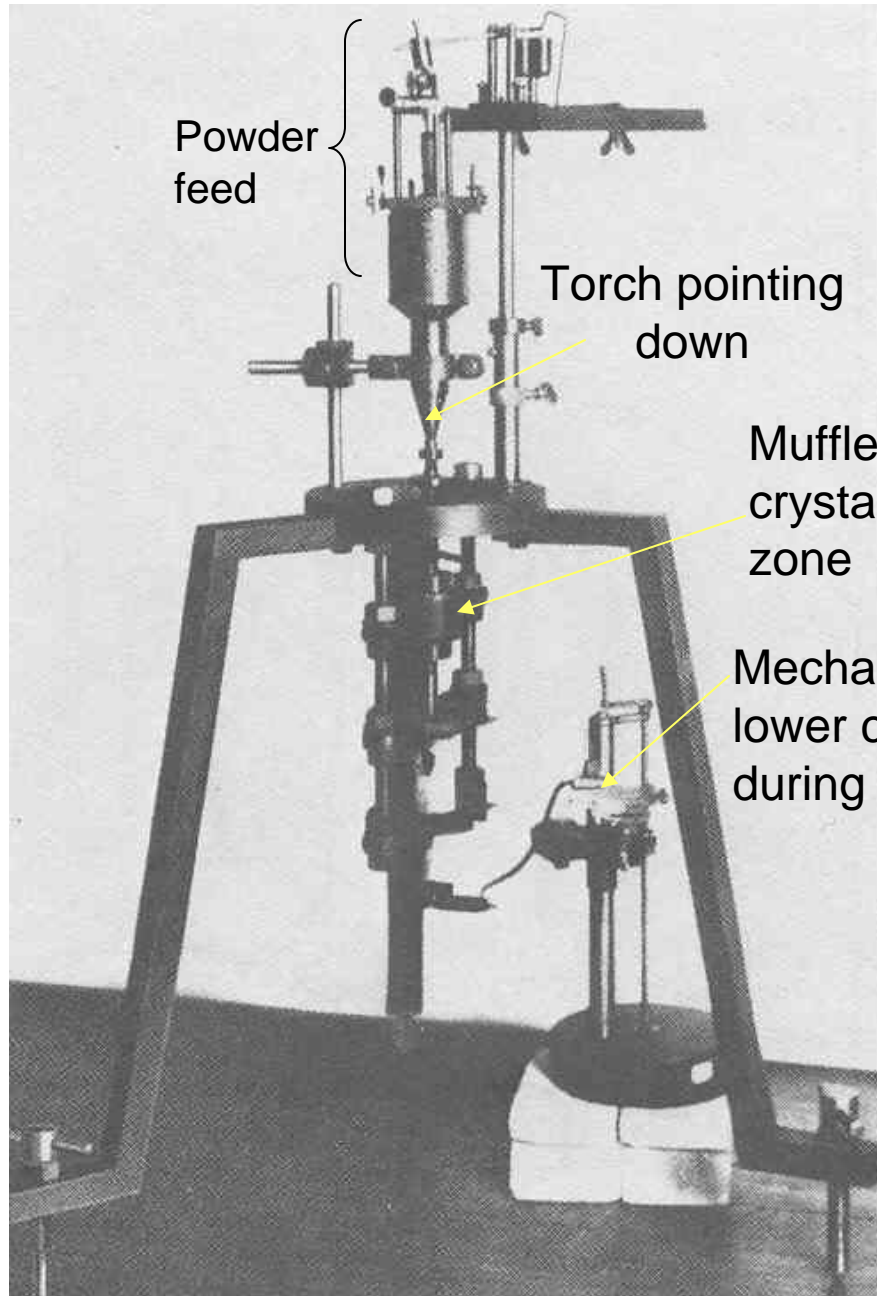
Verneuil Apparatus
US Patent 1,004,505 – September 26, 1911

Inventor
A. V. L. Verneuil by

B. Container filled with feed powder and screen on lower end

$$(NH_4)Al(SO_4)_2 \cdot 12H_2O$$
$$+$$
$$(NH_4)Cr(SO_4)_2 \cdot 12H_2O \xrightarrow{1200°C} \begin{array}{c} Al_2O_3 \\ + \\ Cr_2O_3 \end{array}$$

Recrystallized 4-5×   Feed powder
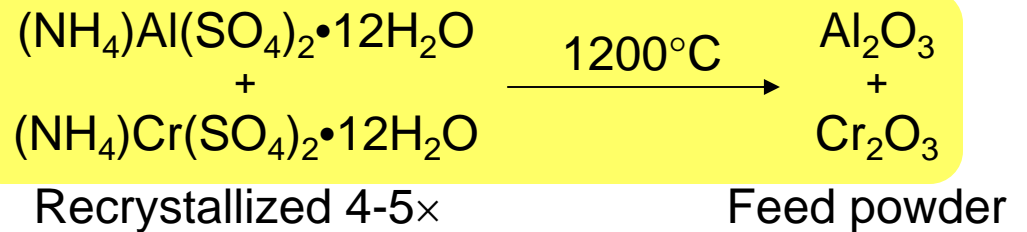
D. Tapping hammer
G. Rotating cam

O. Oxygen inlet
K. Inner tube carries powder plus oxygen
H. Fuel (illuminating gas) inlet
S. Outer tube carries fuel

M. Downward pointing flame
L. Alumina ceramic pedestal held by Pt tube

P. Crank lowers pedestal during growth

Diagram labels: Powder feed · Water cooling jacket · Mica window · Flame and furnace · **Flame** · Mechanism for lowering the growing crystal

Initial fused region where tiny crystal begins to grow

Sinter cone

1   2   3   4   5   6
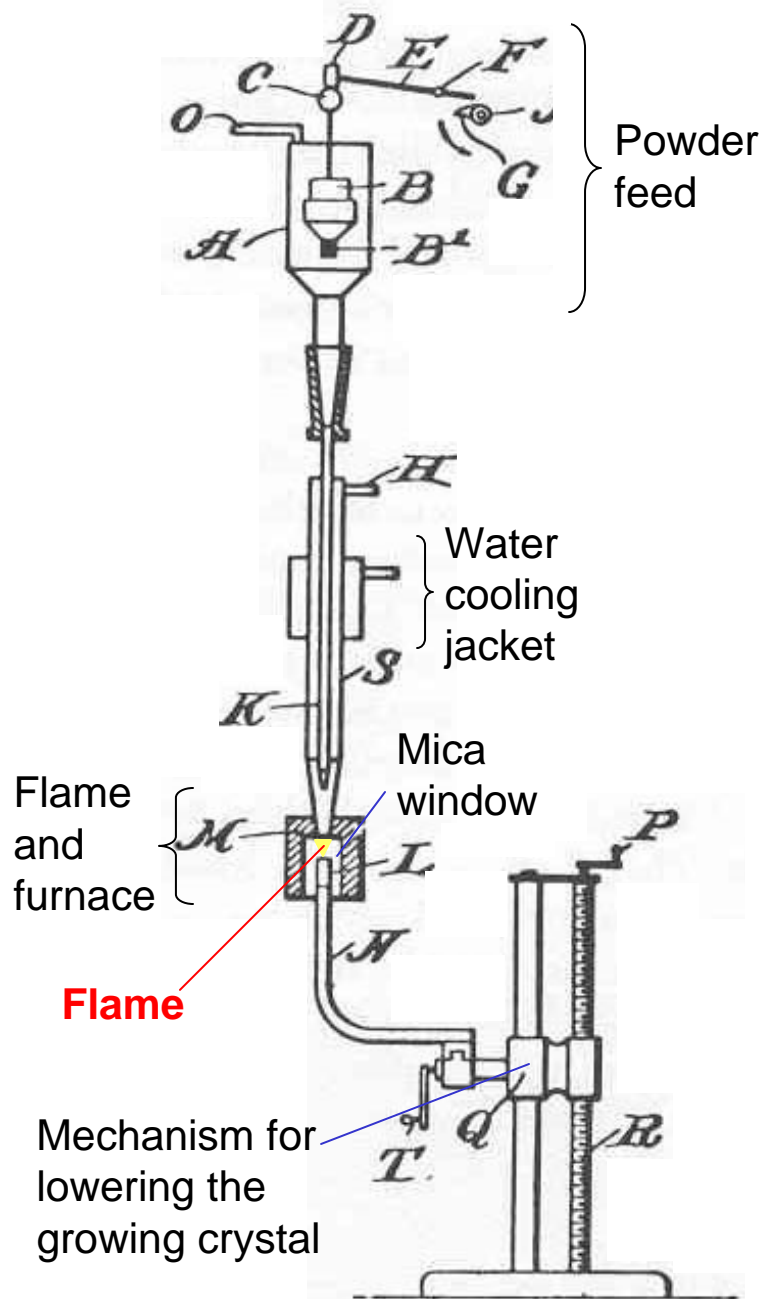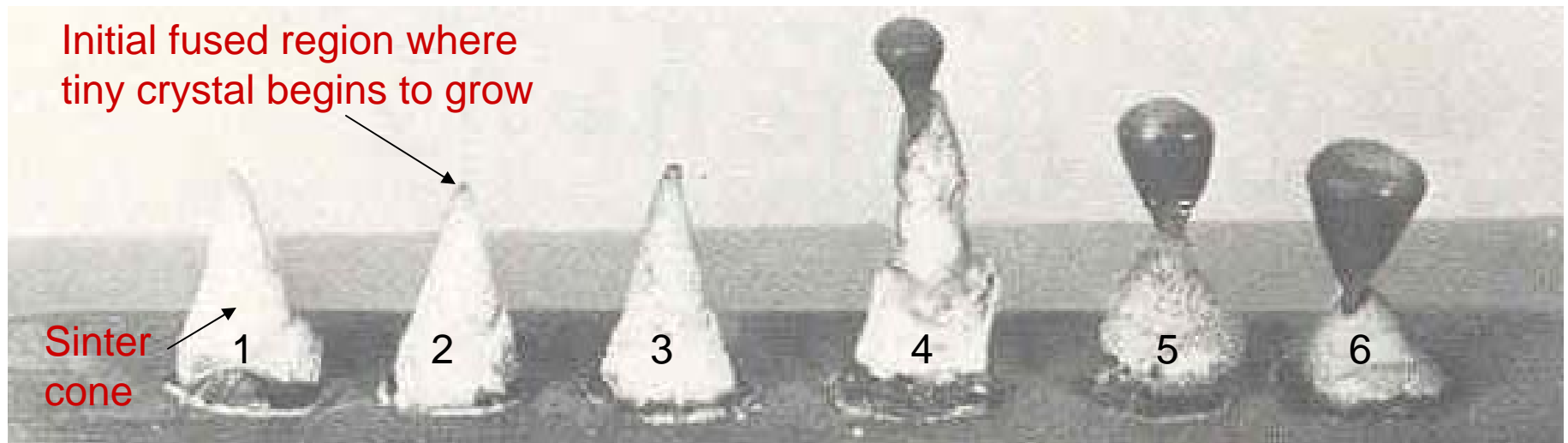
Verneuil-grown ruby in Museum of Arts and Sciences, Paris

Verneuil Flame Fusion Process

1. Hot, almost melted powder falls on alumina pedestal and builds up sintered cone

2. Uppermost tip of cone melts

3. Molten drop enlarges

4. Molten drop enlarges

5. Pedestal is lowered to maintain molten region at constant height

6. Flame shutoff time is critical to avoid cracking
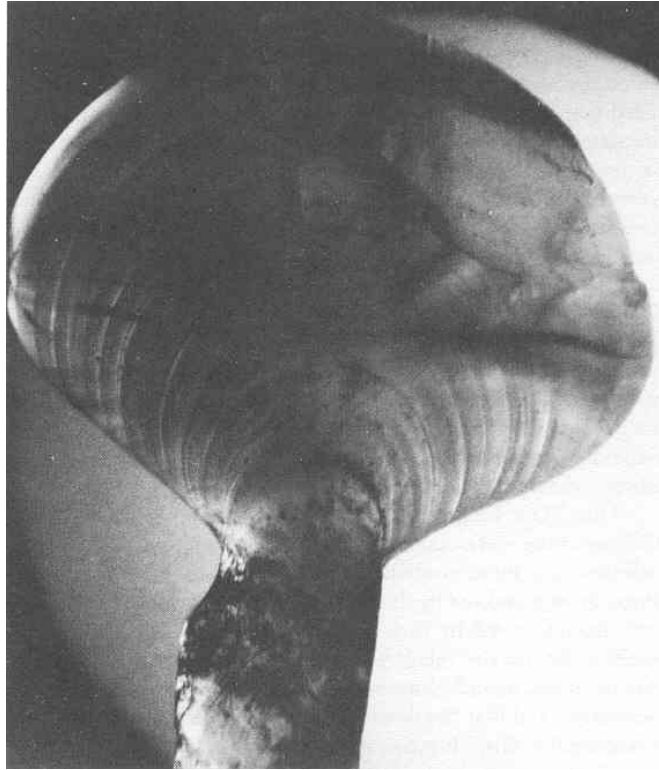
Early Verneuil boule grown
on natural ruby seed crystal
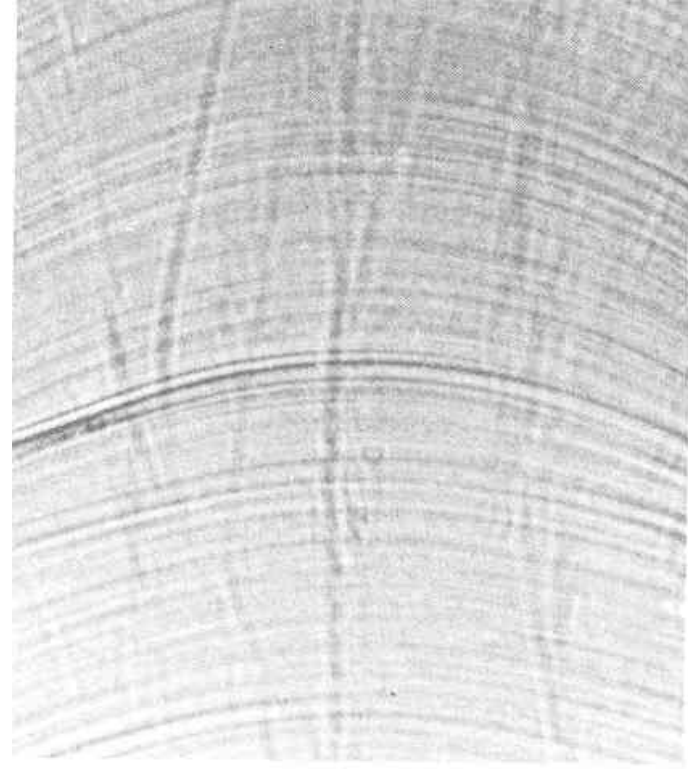
Curved growth striations seen in
almost all Verneuil crystals

Cut Verneuil ruby

Typical ruby boule: tapered cylinder
~25 mm long and 6 mm diameter
weighing 15 carats

After growth, ruby boule is tapped and
it splits in half lengthwise.

First U.S. Synthetic Ruby: Hoquiam Ruby

- 1903-1904: Lumber businessmen Polson and Ninemire set up factory to manufacture ruby in Hoquiam, Washington.

- Kurt Nassau argues that technology was probably provided by one of Verneuil's French assistants.

- Surviving Hoaquiam rubies are low quality material made by Verneuil process. Rubies are small, strained, and have many gas bubbles

- Rubies had to be sent to New York for cutting

- Within a few years, cheaper, higher quality Verneuil ruby from Europe ended the Hoquiam venture.

Auguste V. L. Verneuil
Age 55 in 1911

- 1905: Verneuil becomes Professor of "lime, cement, ceramics, and glassmaking" at National Conservatory of the Arts and Sciences, Paris

- 1909: Verneuil becomes chief chemist in Paris laboratory of L. Heller and Sons of New York (later Heller-Hope Co.)

  Sets up factory to produce ruby and blue sapphire

  By analyzing natural, blue sapphire, Verneuil discovered that the blue color is associated with Fe + Ti impurities

H. W. Friedland ∎ A. A. Heller

A. V. L. Verneuil

I. Spec-Torsky

I. H. Levin
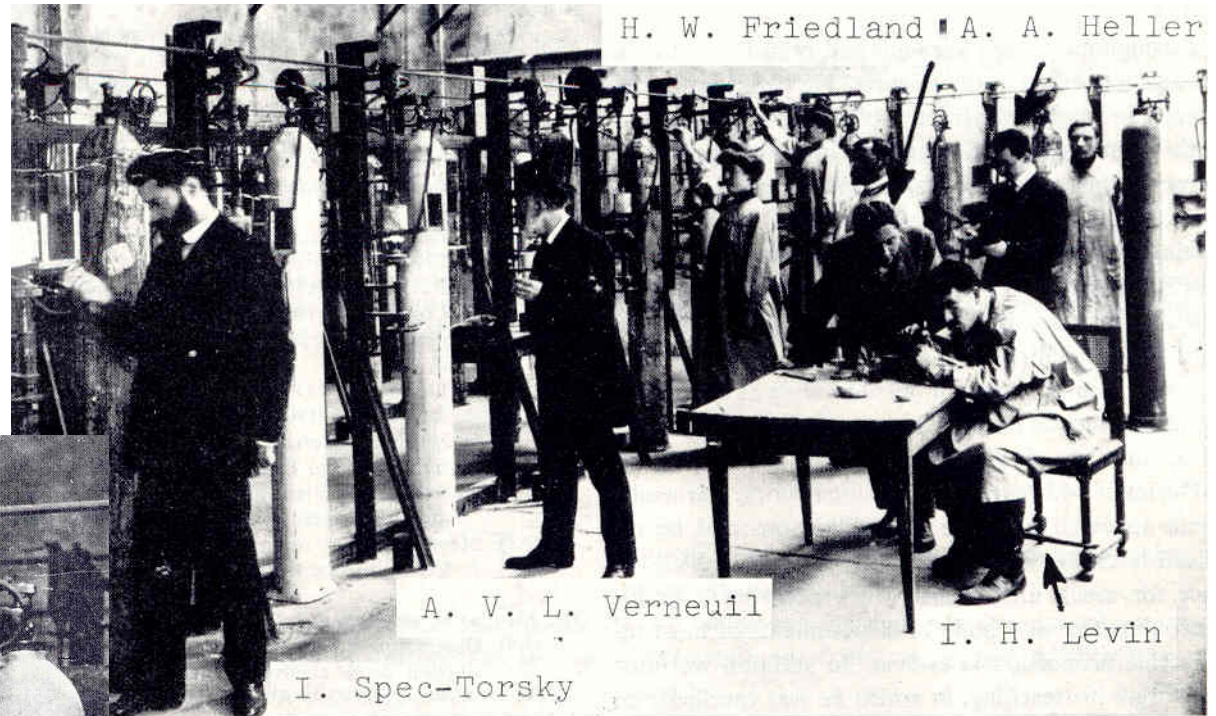
Heller Laboratory in Paris, 1910 with Verneuil torches

By 1907, several manufacturers were producing synthetic ruby at a total rate of 5 million carats/yr
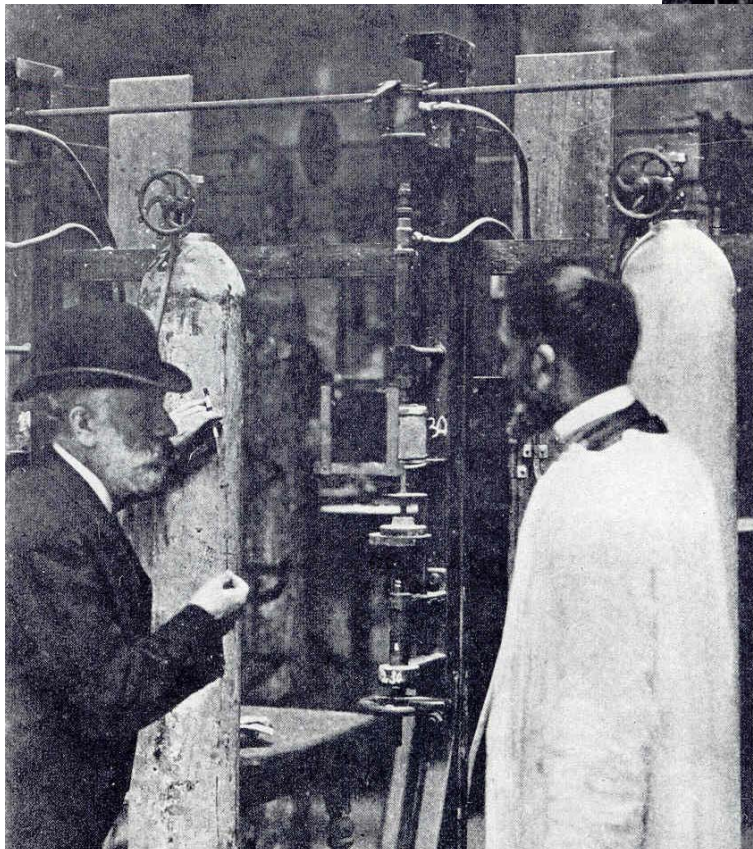
Prof. Verneuil

Verneuil growth room with almost 100 torches in 1920

Industrie de Piérres Scientifiques, Hrand Djévahirdjian, Switzerland
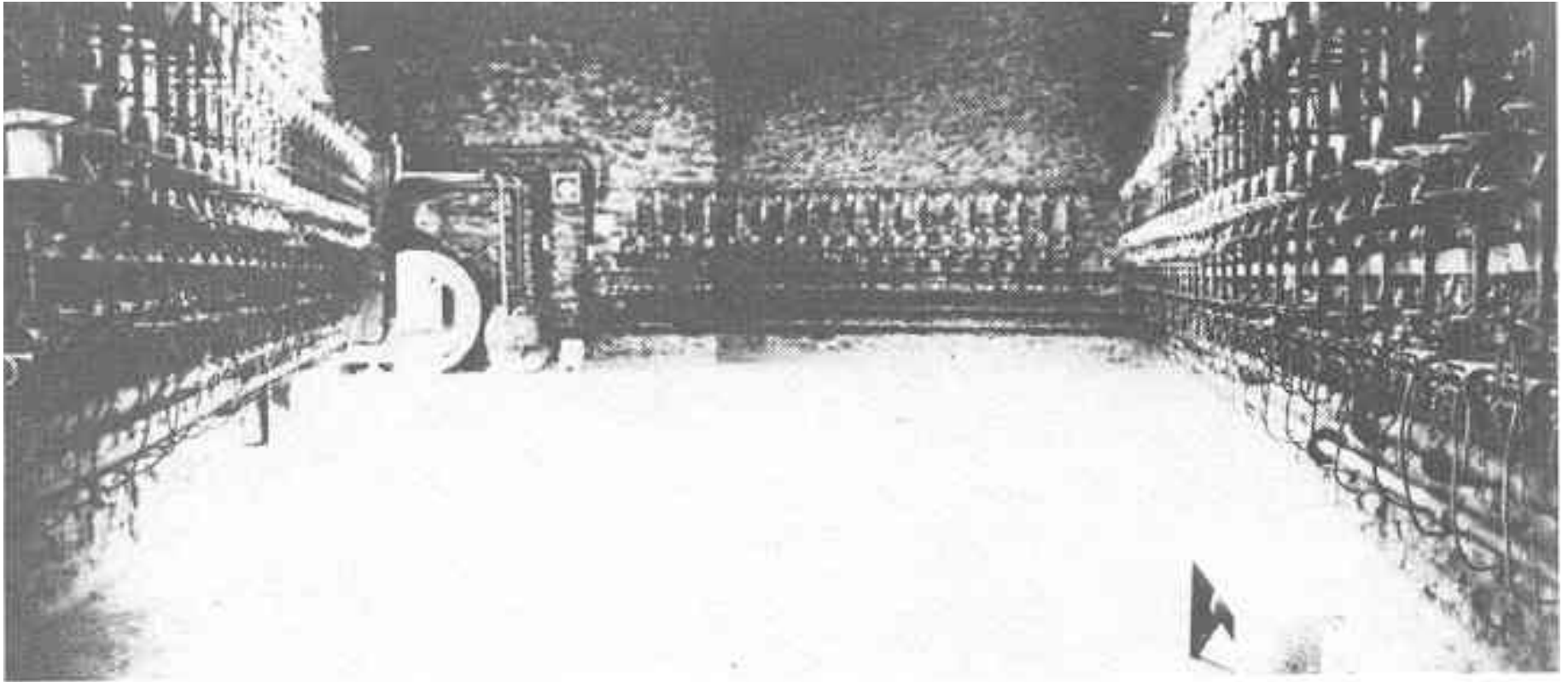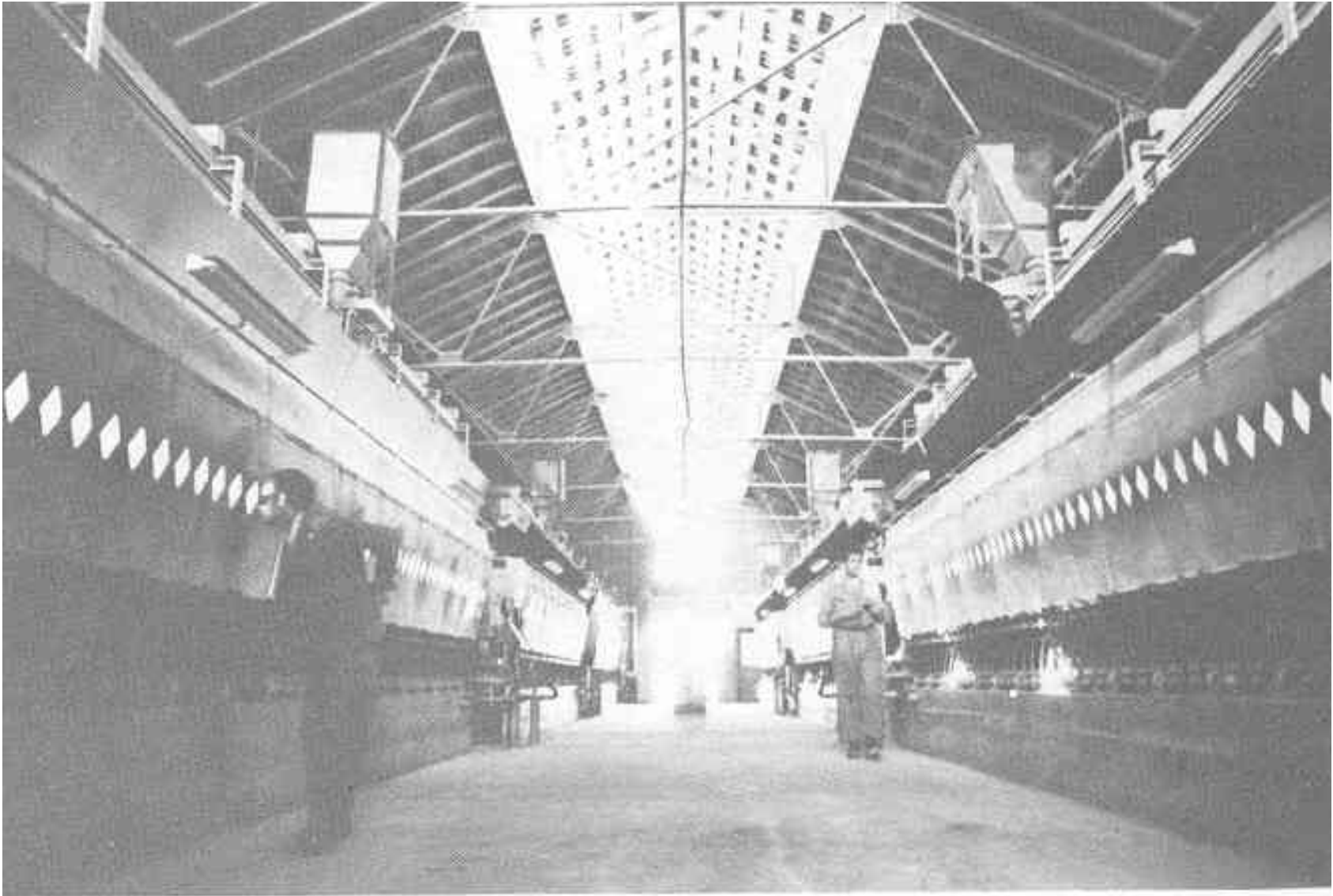
Verneuil Growth Room of Djévahirdjian
Plant with 270 Torches (~1970s)

Savva K. Popov: Soviet Pioneer in Ruby and Sapphire Growth

Institute of Crystallography, Academy of Sciences of USSR

S. K. Popov (1903-1953)

1932: Began work on Verneuil crystal growth

1938: Produced semi-automatic growth apparatus to make long thin rods suitable for watch jewels

1945-50: Improved device for making ruby rods

1951-53: Developed new use for corundum rods
- fiber guide for making artificial fibers
- flame polishing of corundum
- method of bending corundum rods

1959 assessment by N. N. Sheftal':
Popov made more uniform crystals by optimizing feed and heating conditions. Equipment and crystal quality better than those in Western Europe

S. K. Popov in *Growth of Crystals* (A. V. Shubnikov and N. N. Sheftal', eds), Chapman & Hall, London, 1959, pp 104-135

Popov's work

50 mm

Ruby boules circa 1950

1939

1950

S. K. Popov in *Growth of Crystals* (A. V. Shubnikov and N. N. Sheftal', eds), Chapman & Hall, London, 1959, pp 104-135
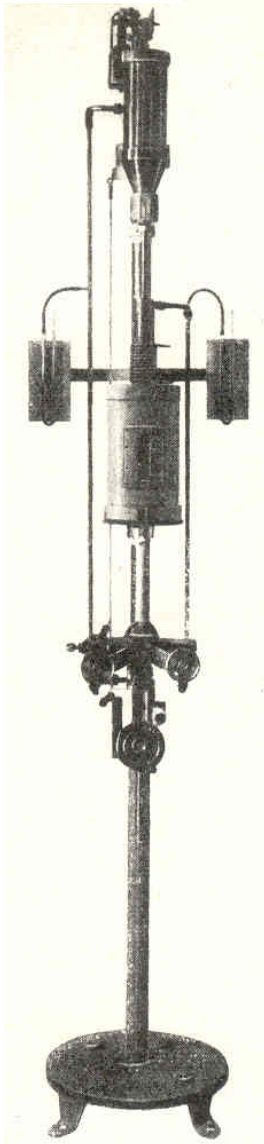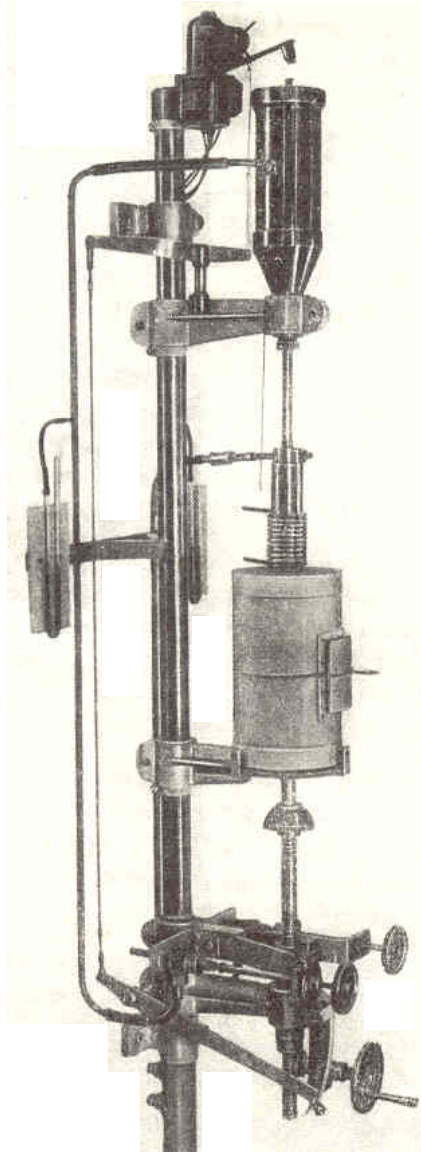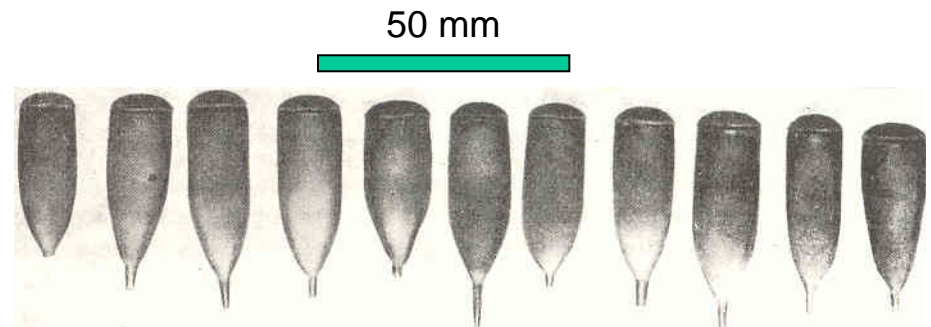
Linde Air Products Co. Verneuil Ruby and Sapphire in U.S.

- No synthetic ruby/sapphire production in U.S. after Hoquiam

- With European sources of jewel bearings cut off in World War II, U.S. government issued development contracts

- Linde Air Products Co. begins Verneuil production in East Chicago, IN. Linde was a compressed gas producer

- After World War II, Linde could not compete with lower European labor costs. Linde developed automated process for making 81 cm x 5 mm rods that could be efficiently cut into jewel bearings
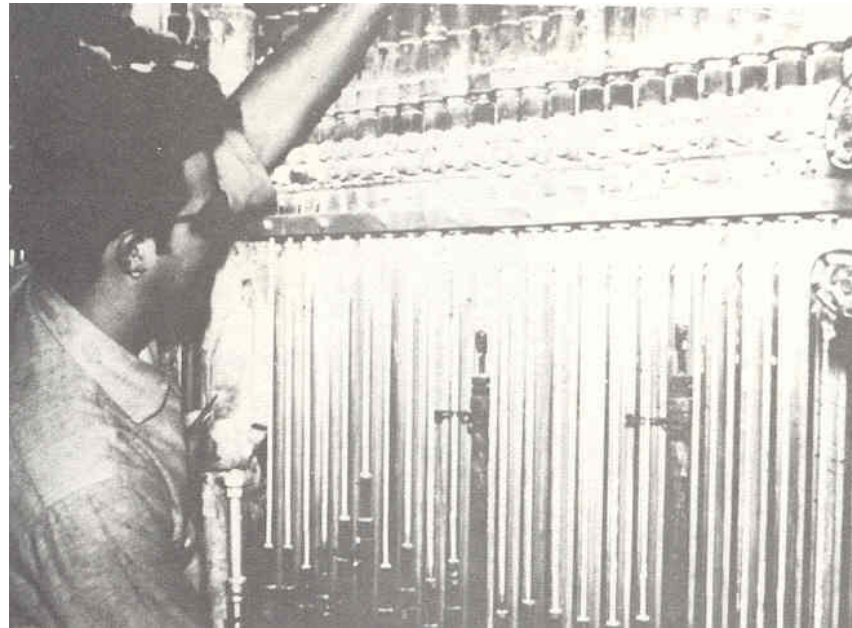
Linde Verneuil growth in 1960

Verneuil Crystal Growth in 1979

GROWTH AXIS [0001]

GROWTH AXIS [224̄3]

GROWTH AXIS [11̄2̄0]

[0001]

60°

[11̄2̄0]

[101̄0]

[11̄2̄0]

[0001]

0° CRYSTAL

60° CRYSTAL

90° CRYSTAL

Corundum grown along different crystal directions has different cross sections
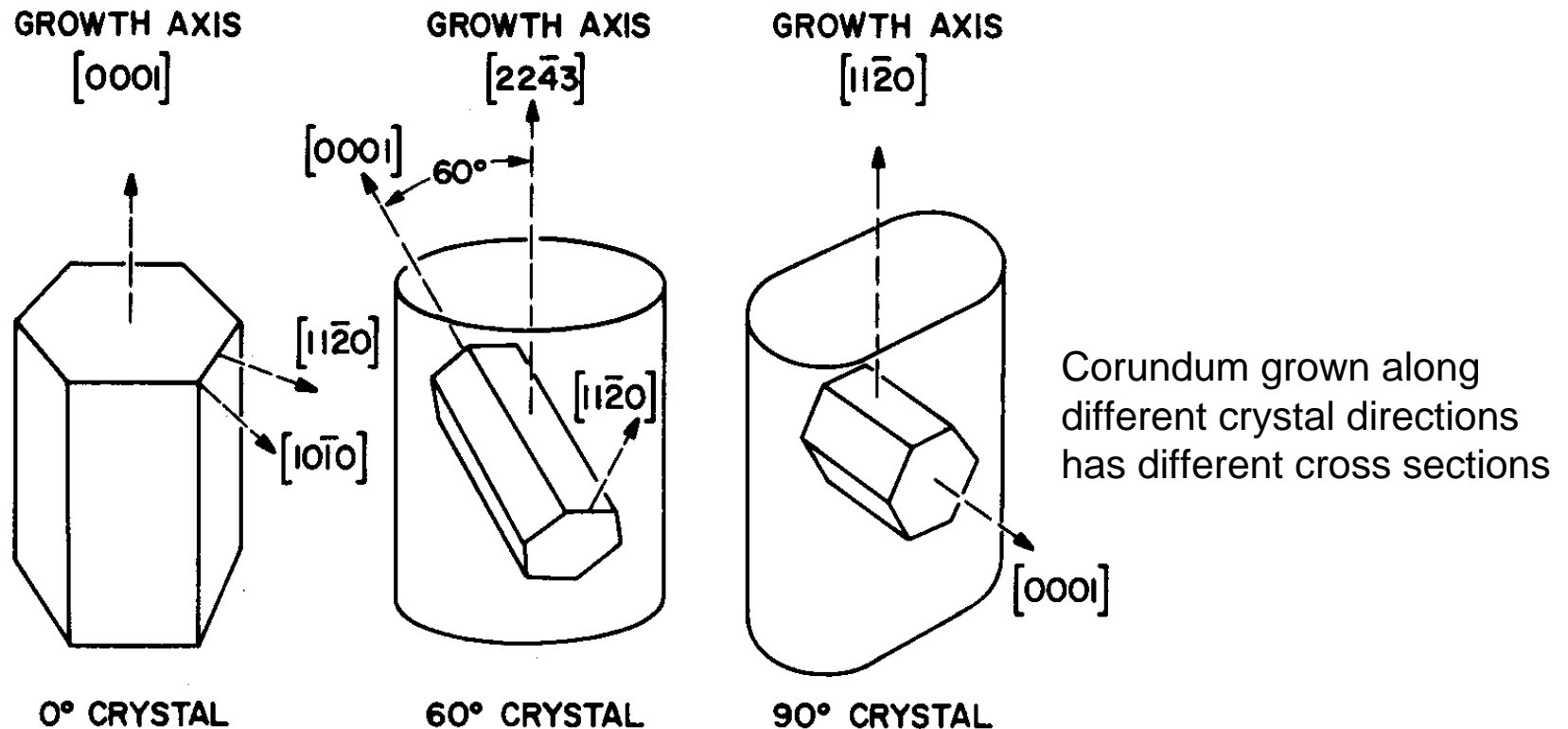
- Partial melting of feed powder occurs in flame, with complete melting only in thin layer on top of boule. 30-40% of feed powder is lost and cannot be re-used.

- Boule is lowered at 1 cm per hour

- Flame is shut suddenly at end of run. "If the boule does not shatter in the next ten seconds, then the remaining stress will be relieved by a light tap with a hammer, which causes the boule to split in half."

1960: Demand for Ruby Crystals for Lasers Spurred Development of Larger Verneuil Boules and Eventually Led to Czochralski Crystal Growth

43-cm-long Linde Verneuil ruby weighing 4500 carats

120-carat ruby from Linde

19-cm-long early Czochralski ruby from Linde
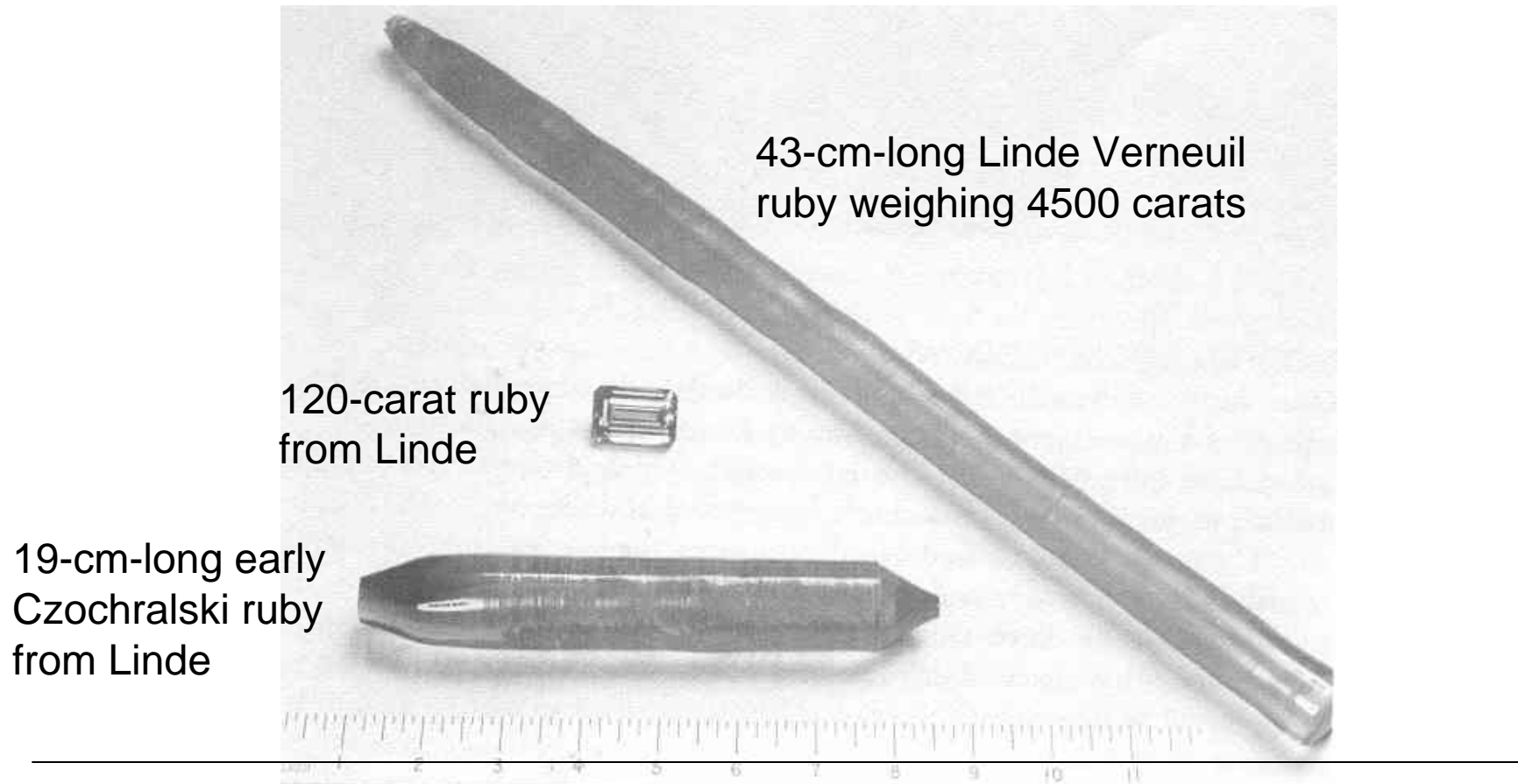
1974: Linde East Chicago facility closes and U.S. ruby growth ceases

Linde Crystal Products Division becomes part of Union Carbide and focuses on Czochralski growth

Czochralski Crystal Growth of Corundum

- In 1979, Verneuil ruby and sapphire was least expensive variety and was used for gems, watch and instrument bearings, thread guides in weaving machines, balls in ball-point pens, and phonograph needles (remember those?)

- Higher crystal quality was needed for lasers

- Czochralski crystal growth

  - Pure Al_2O_3 is melted in iridium crucible just above 2050°C

  - Sapphire seed crystal is dipped into melt. If temperature is too low, melt crystallizes. If temperature is too high, seed melts.

  - Seed is rotated (up to 30 rpm) and pulled out of melt at 6-25 mm/h

  - Atmosphere is typically 98%N_2-2%O_2

  - Careful control of pull rate required for constant diameter boule

  - 11-cm-diameter crystals can be pulled from 15-cm crucible
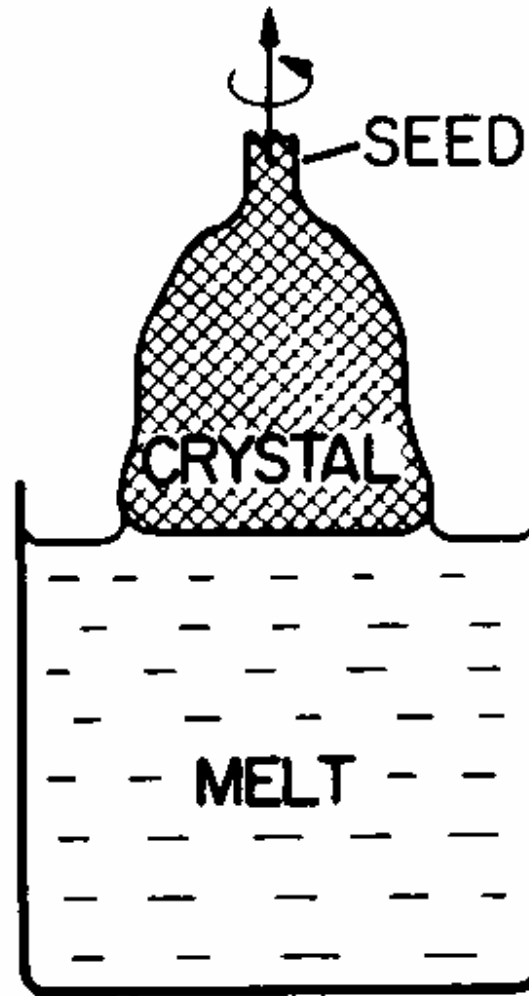
Union Carbide Czochralski Crystals

4.2 kg ruby

10 kg sapphire

Czochralski sapphire applications in 1980s:

Infrared and ultraviolet windows
Windows for xenon lamps
Sodium lamp tubes
High-pressure cell optics
Photomultiplier tube face plates
Ultracentrifuge cell windows
Corrosion-resistant cells, crucibles, tubes
High-power laser optics
Semiconductor wafer carrier plates
Photomasks and plates
Radiation light pipes
Transparent electronic substrates
Optical flats
Microwave output windows
High-temperature process windows

---From Union Carbide product literature

Union Carbide Sapphire Plant in
Washougal, Washington, 1988

1999:   Union Carbide Crystal Products Division acquired by Bicron.
        Bicron was the successor to Harshaw Chemical Co, a
        producer of optical crystals. Bicron had been acquired by
        Saint-Gobain in 1990.

2000:   Sapphire division renamed "Saint-Gobain Crystals and
        Detectors"

2003:   Czochralski sapphire is still produced at Washougal plant

EFG Growth Method: **E**dge-Defined **F**ilm-Fed **G**rowth

Nassau,
*Gems Made
by Man*
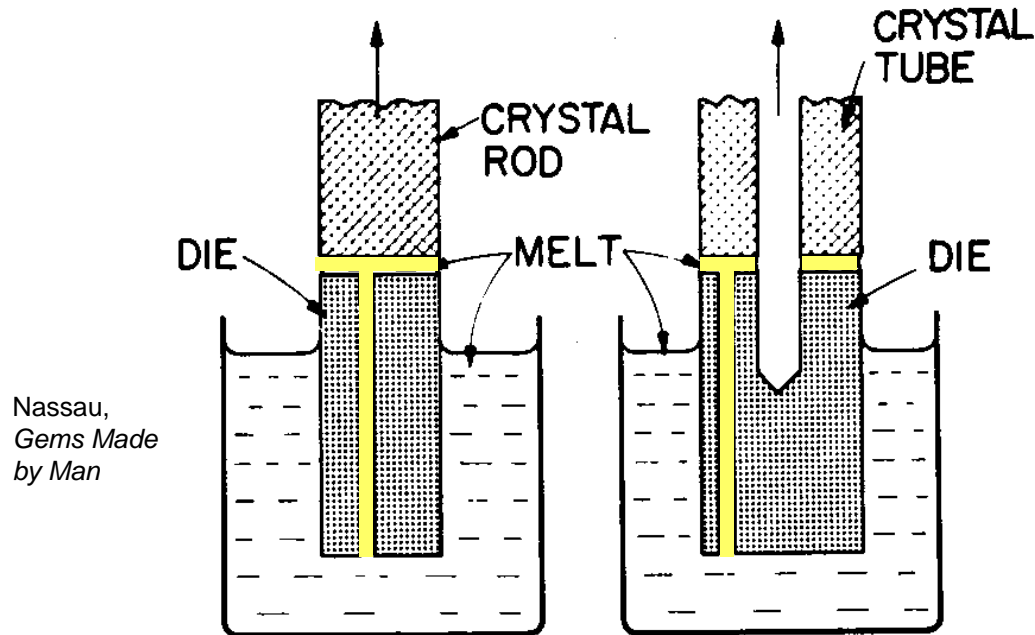
- Melt Al_2O_3 in molybdenum crucible
- Melt wets surface of molybdenum die and moves up by capillary attraction
- Dip sapphire seed crystal into melt on top of die
- Pull seed crystal to draw out crystallizing Al_2O_3
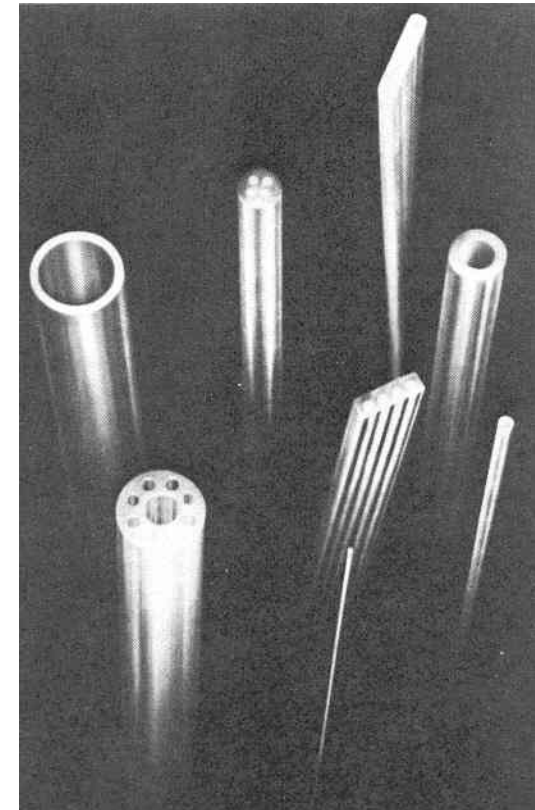
EFG-drawn sapphire
(Tyco Labs)

- Research at Tyco Laboratories, Waltham, MA, funded by Air Force in 1965 to develop EFG continuous sapphire filament for reinforcement of metal matrix composite (Report AFML-TR-66-246,1966)

- EFG method invented at Tyco by Harold E. LaBelle, a technician without a college education. Patent issued to LaBelle in 1971

Genesis of EFG Crystal Growth

Tungsten seed

Growing sapphire

Liquid alumina

Tungsten heater

Sapphire crystal filament

Molybdenum orifice
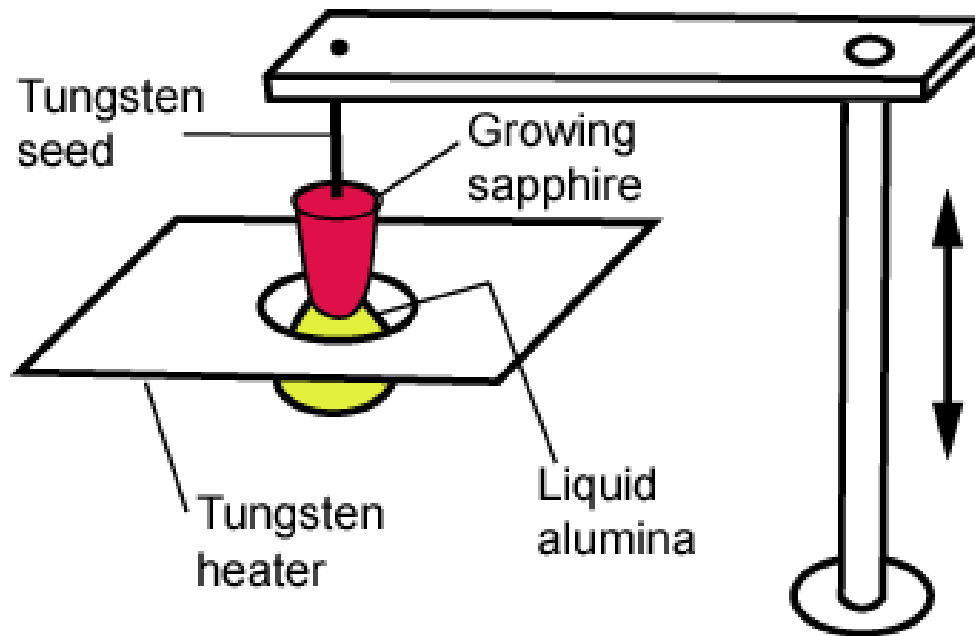
Liquid

1. Czochralski-like growth of sapphire from molten alumina using tungsten wire as a "seed crystal". Diameter of crystal is related to diameter of remaining liquid drop
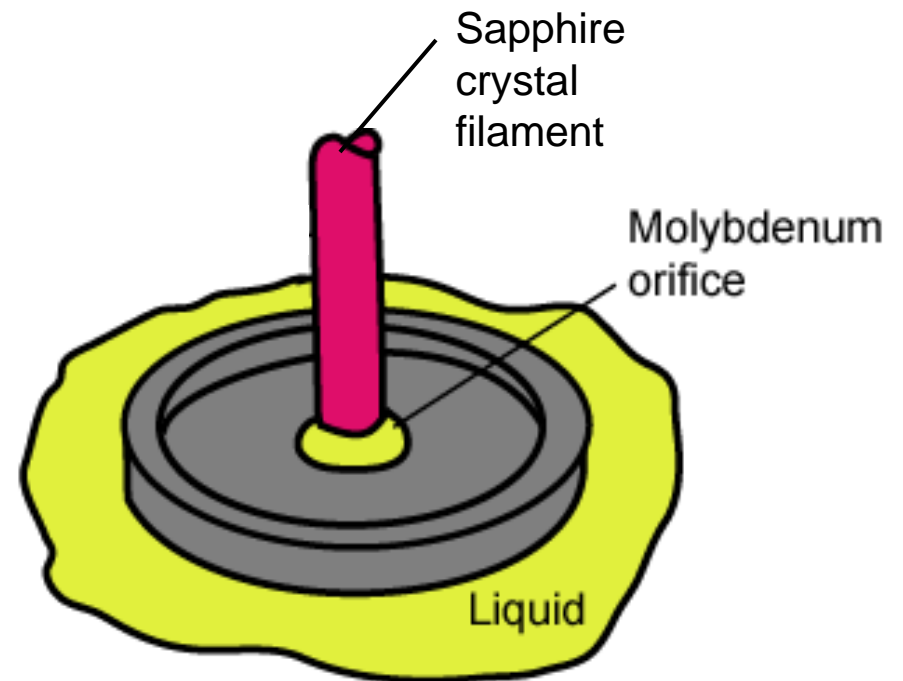
2. Floating orifice: Mo washer floats on liquid alumina. Diameter of crystal filament is governed by diameter of orifice. Method is not stable enough for manufacturing.

Genesis of EFG Crystal Growth
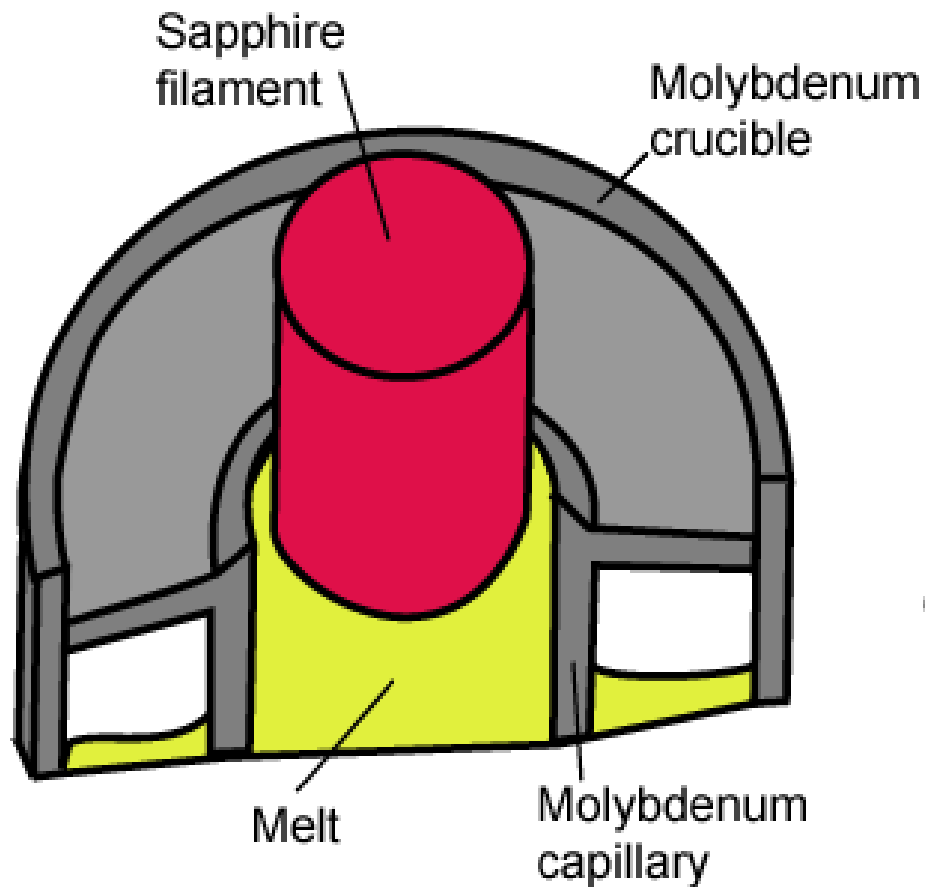
3. Self-filling capillary tube for sapphire filament growth. Mo no longer floats on melt
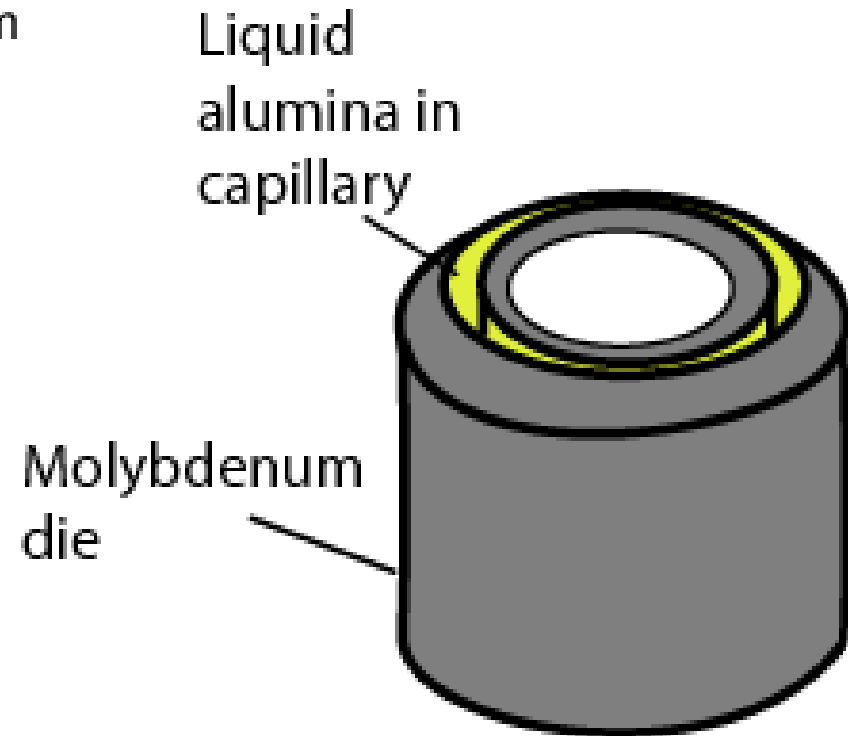
4. Self-filling capillary for growth of sapphire tube

Genesis of EFG Crystal Growth
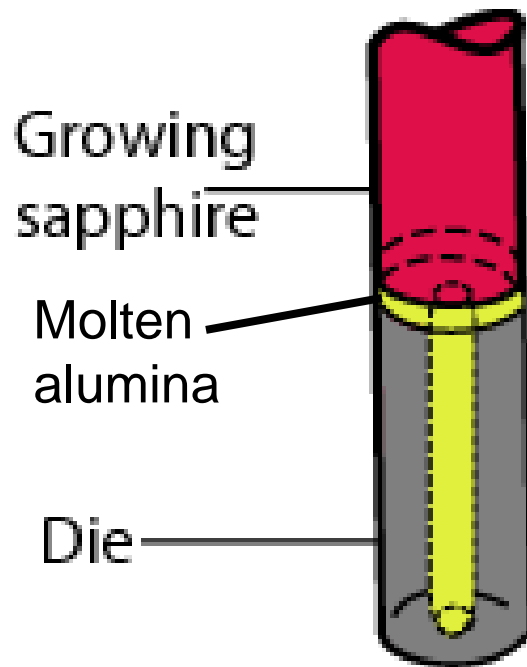
5. First Edge-Defined Film-Fed Growth of sapphire filament. Diameter of die, not diameter of melt column, dictates diameter of filament
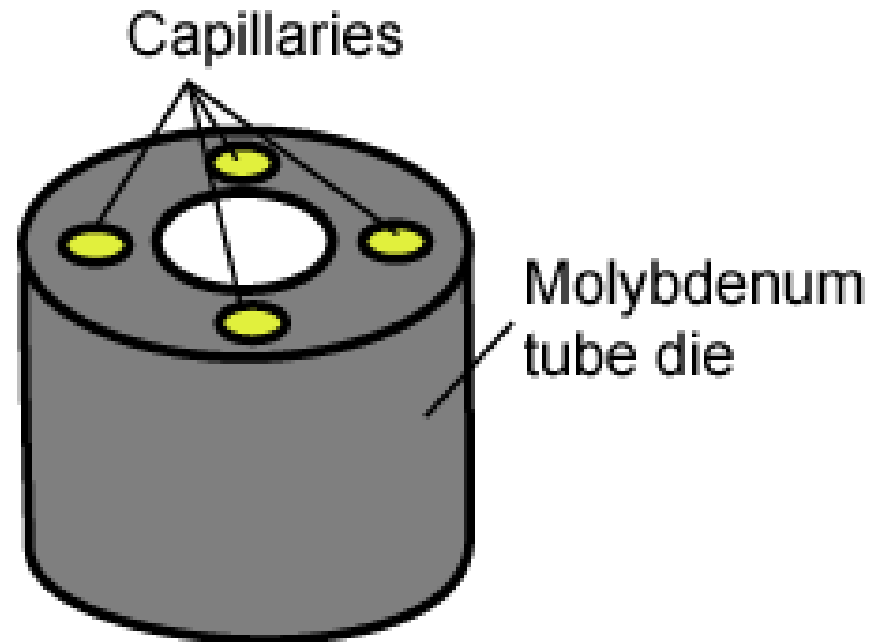
6. Experiment proved that the edges of the Mo die defined the edges of the sapphire crystal.

- LaBelle suggested the name "continuous shaped film propagation"
- His boss, Ed Mlavsky, called it "edge-defined film-fed growth"

Saphikon Company History

Early EFG Sapphire

- 1970: Tyco Laboratories created Saphikon Division in Waltham MA and moved it to Milford NH 1978

- 1970s-1980s: Saphikon revenue mainly from licensing EFG technology to companies such as Kyocera, RCA, Corning, Allied Signal. Licensees saw potential for silicon-on-sapphire products

- 1982: Tyco president Joe Gaziano dies and John Fort becomes president

- Saphikon Division had less than $2M/yr revenue. Fort tried to sell Saphikon but found no taker

- Fort sold Saphikon to Harry LaBelle in 1985 in a deal "too good to refuse". LaBelle's intention was to resell Saphikon

- 1985: Department of Energy funded project for optical fiber for high temperature and corrosive conditions

- Saphikon purchased by Cy Gregg in 1987. Tim Davis was President/CEO in 1990s

- 2000: Saint-Gobain buys Saphikon to manufacture sheets, rods, tubes, 3-dimensional shapes. Gregg forms Photran which retains exclusive right to manufacture sapphire fibers (for optical and structural applications)
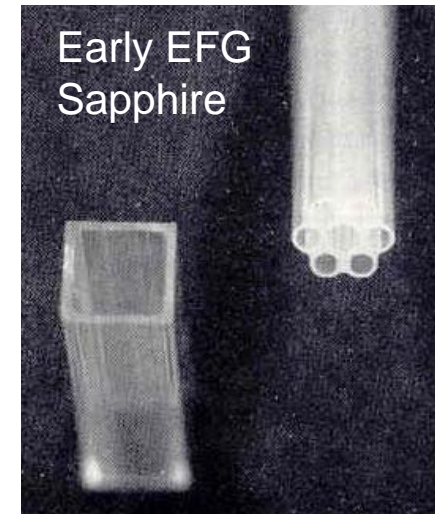
Saphikon EFG Sapphire Sheets
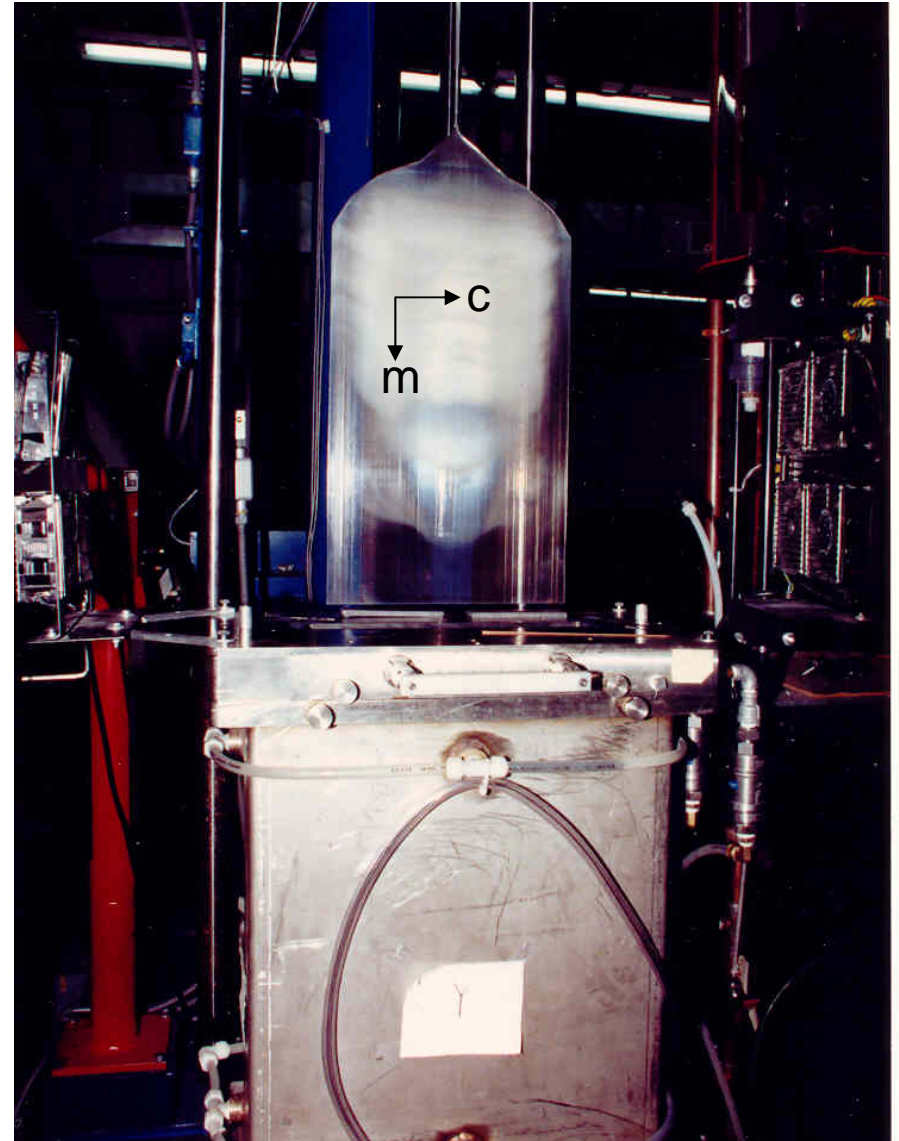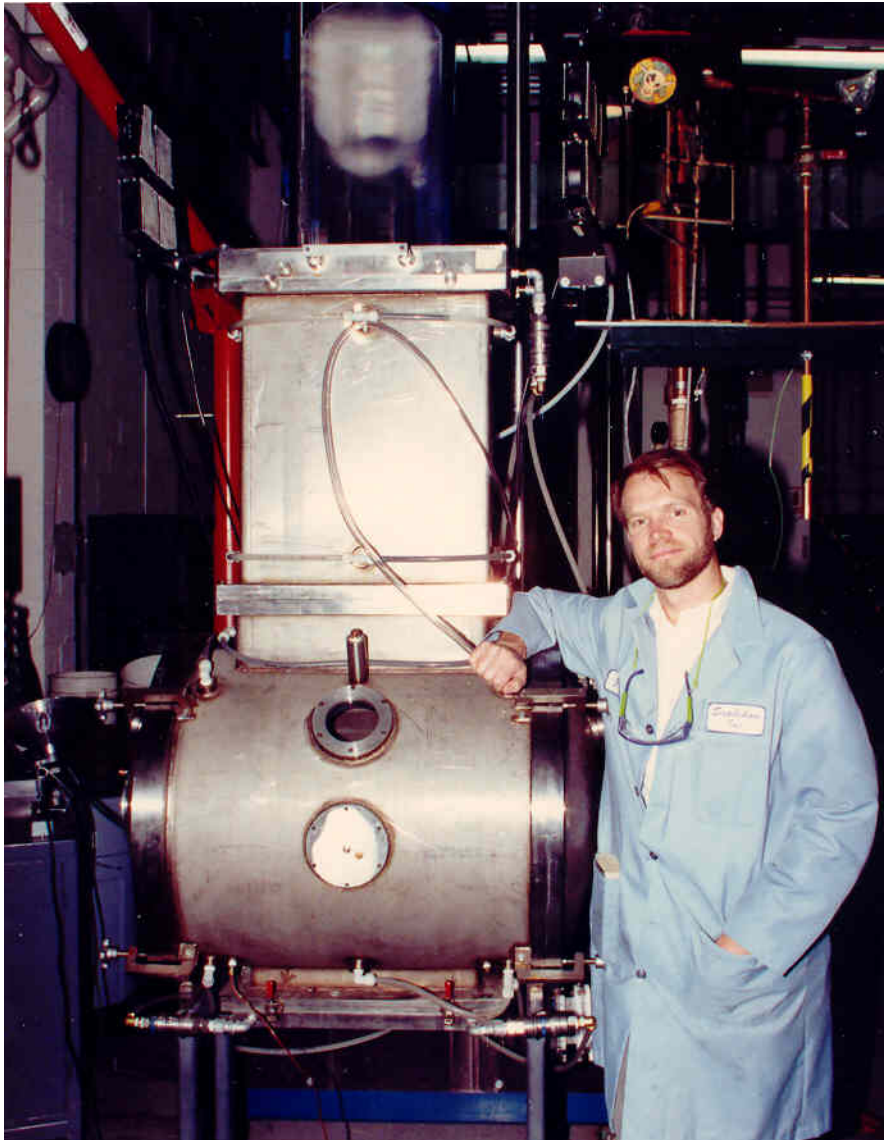
- EFG sapphire fiber uses
  - Optical fibers for Er-YAG lasers for medical use
  - Proprietary structural composites
    (Fibers grown for ceramic/ceramic composites
    for National AeroSpace Plane in 1980s)

- EFG bulk sapphire uses
  - Bar code scanners - largest application
  - Substrates for blue LEDs and laser diodes
  - Semiconductor manufacturing equipment
    Tubes for plasma applicators
    Windows for high temperature/corrosive environments
    Electrostatic chuck to hold wafer in place during processing
    End effector on robotic arm - grabs wafer and moves it during processing
  - Laser material
  - Scalpels and ceramic parts used inside the body
  - Infrared sensors components

- Kyocera EFG sapphire products available in 2003
  - r, a, or c-plane sheets up to 20 cm wide x 30 cm long x 0.02-2 cm thick
  - c-axis rods 0.05 to 2 cm diameter up to 1 m long
  - c-axis tubes
  - Violet sapphire jewels

Green
traffic
light

Information from Cy Gregg, Tim Davis and Kyocera web site

Stepanov Independently Developed Shaped Sapphire Crystal Growth in USSR in 1960s

Seed
Edge definer
Molten charge
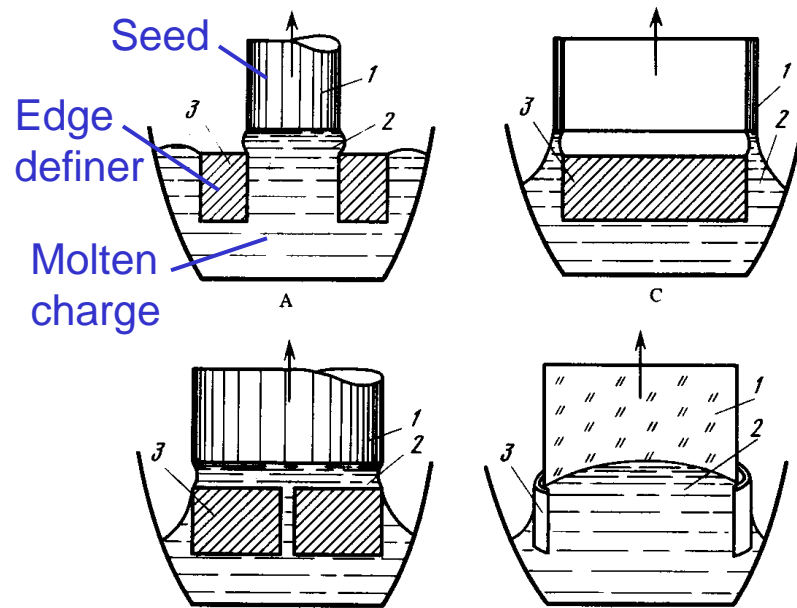
Growth of shaped corundum began in early 1970s
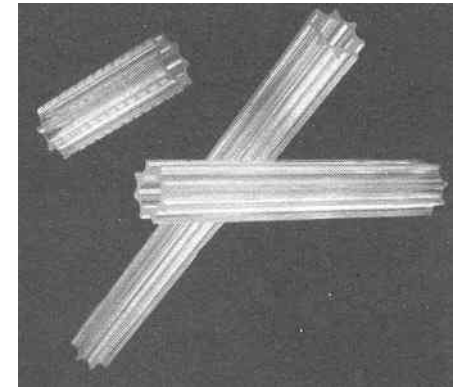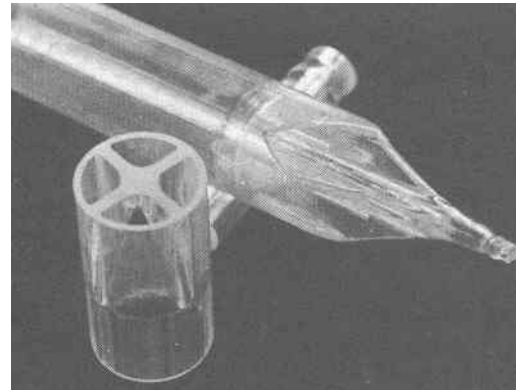
Effusion cells for molecular beam epitaxy
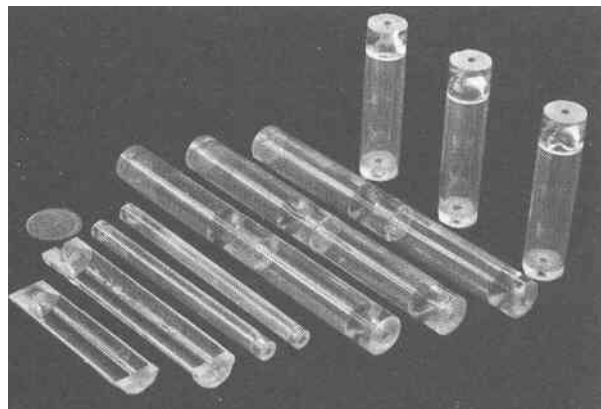
Sodium lamp envelops and boats for making ultrapure materials
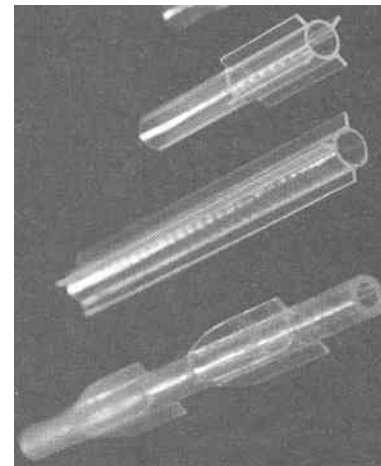
P. I. Antonov in *Growth of Crystals*, Vol 13 (E. I. Givargizov, ed), Plenum, New York, 1986; V. A Borodin et al. in *Growth of Crystals*, Vol 15 (E. I. Givargizov and S. A. Grinberg, eds), Plenum, New York, 1988

36

Difference Between Stepanov and EFG Crystal Growth
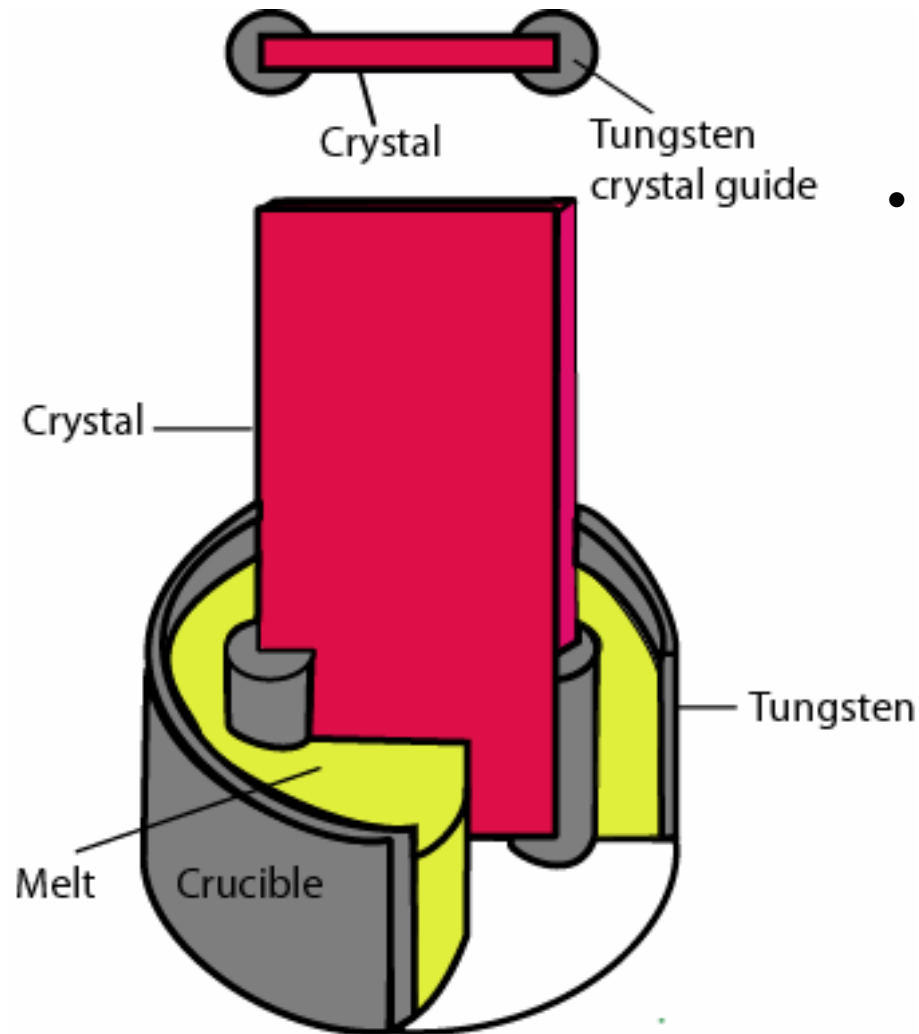
Stepanov Crystal Growth

EFG Crystal Growth

- Stepanov method: wettable or nonwettable aids shape the melt column which shapes of the crystal

- EFG: shape of die, not shape of melt column, controls shape of crystal
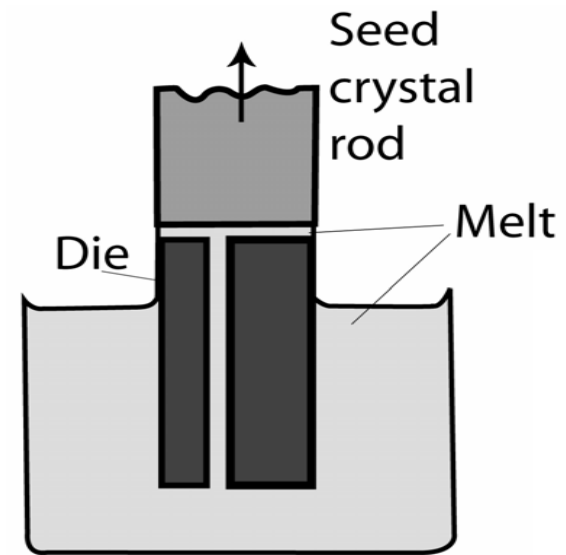
Sapphire Growth by Heat-Exchanger Method (HEM)
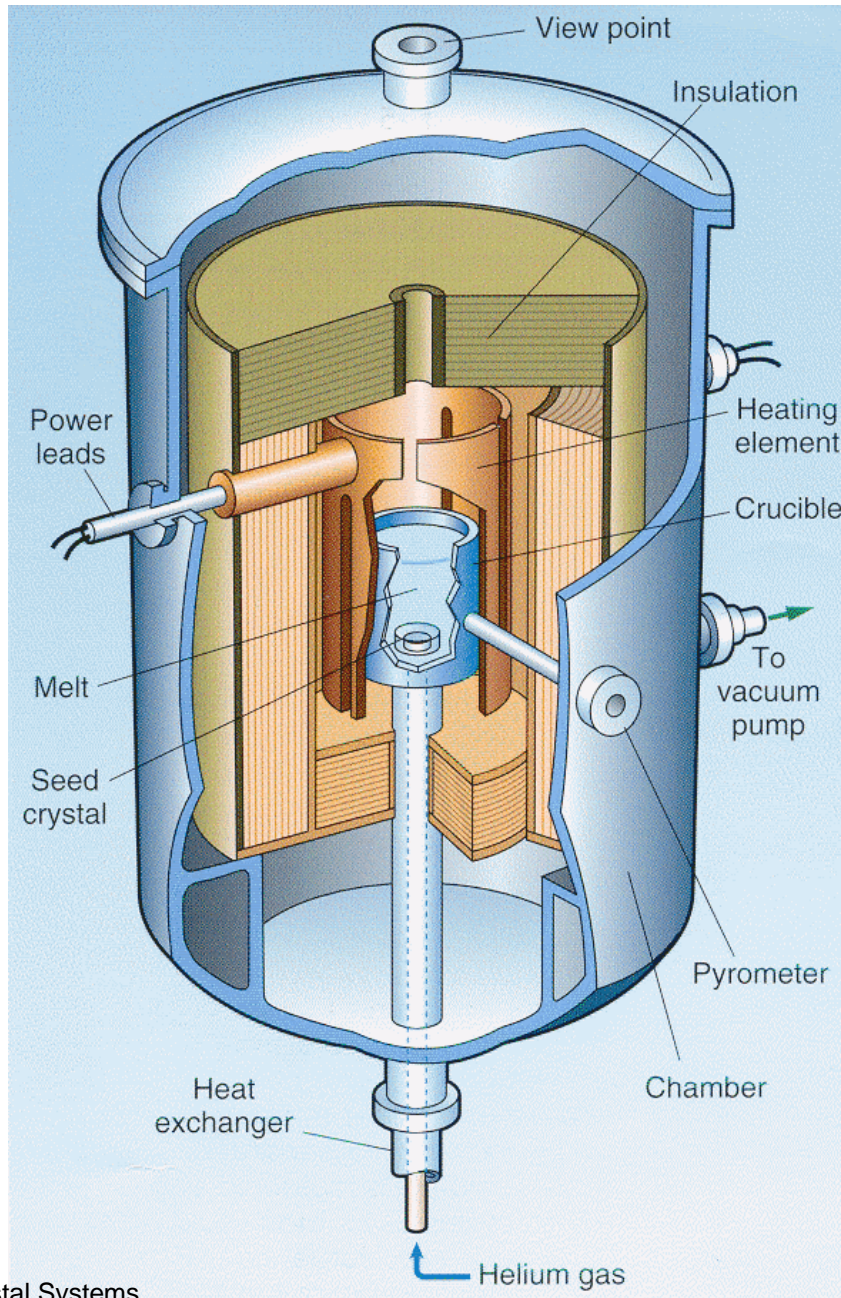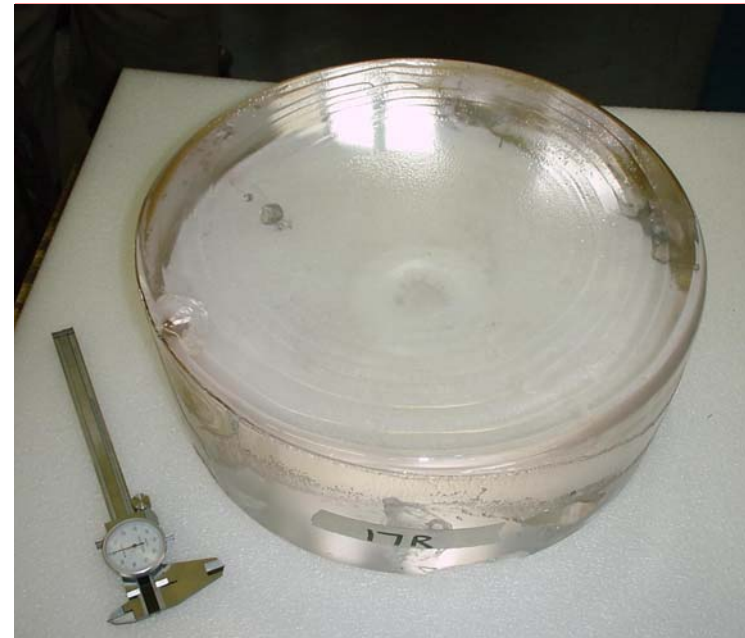
- Crucible with seed crystal at bottom is loaded with Verneuil crackle
- Evacuate and heat to melt charge. Seed is cooled by He flow through heat exchanger
- After some melting of seed, increase flow of He to initiate crystal growth
- When solidification is complete, decrease He flow and anneal in situ by slow cooldown

Crystal Systems

Origins of the Heat Exchanger Method

Fred Schmid and Dennis Viechnicki
in early days of HEM development
at Army Materials Research Lab in 1960s

- Early 1960s: Lafayette mechanical engineer Fred Schmid worked in manufacturing at Watertown Arsenal
  - Directional solidification of metals
  - He-cooled arc furnace for casting Ti

- After Arsenal closed, Schmid worked for precision casting company and decided to go to Northeastern for MS in Materials Science

- 1967: Schmid returned to AMRL and conceived He-cooled heat exchanger. Worked with D. Viechnicki on directional solidification of alumina

- 1967: single-xtal Al_2O_3 in 3/4″ crucible

- 1969: crack-free 3″ xtal after 50 tries

- 1969: first HEM patent issued

- 1971: 6″ diameter boule grown

Growth of Sapphire Disks from the Melt by a Gradient Furnace Technique

F. SCHMID and D. VIECHNICKI
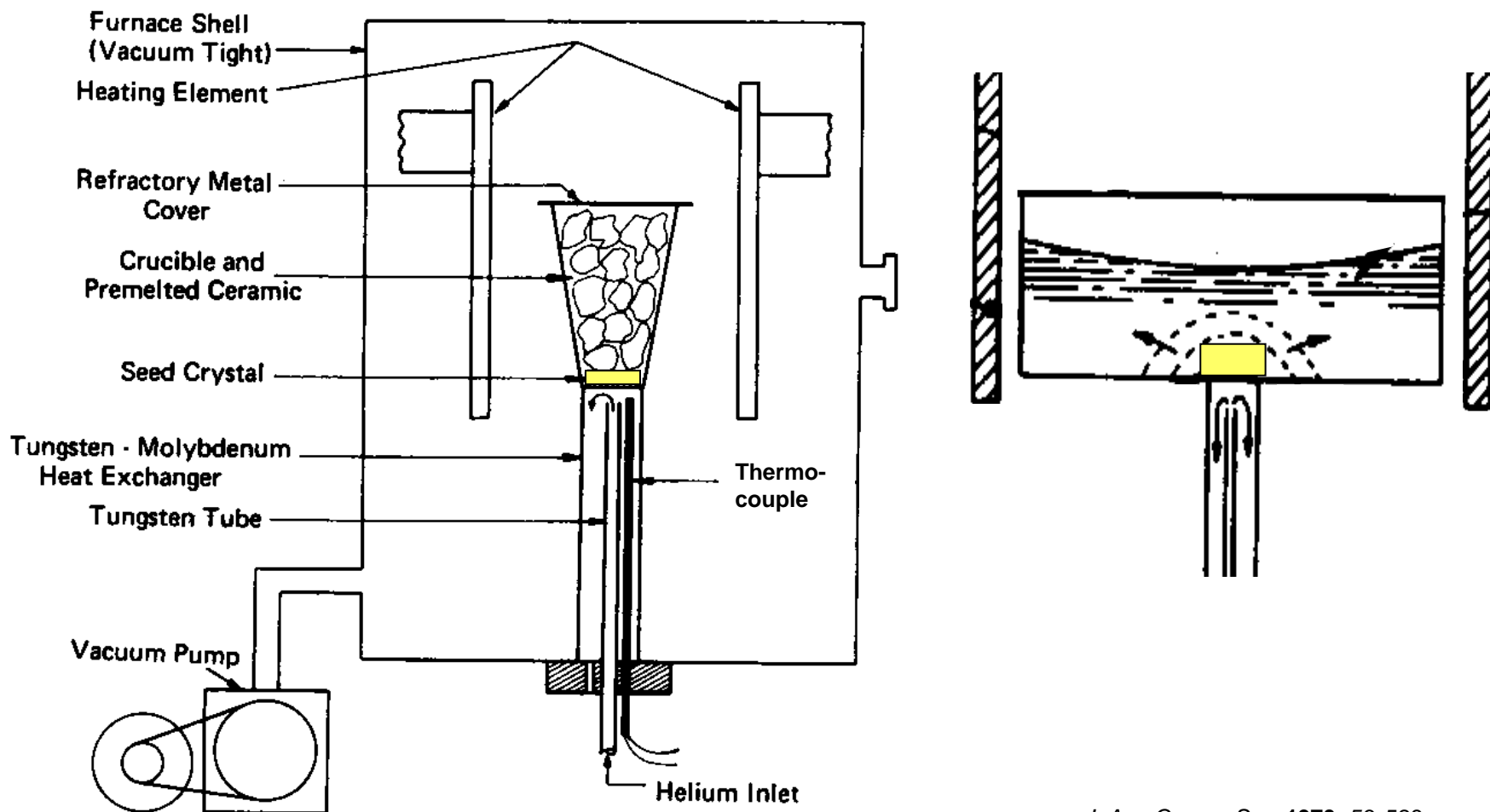
First sapphire grown in Watertown

Larger boule in crucible

PROGRESS OF SAPPHIRE SINGLE CRYSTAL GROWTH
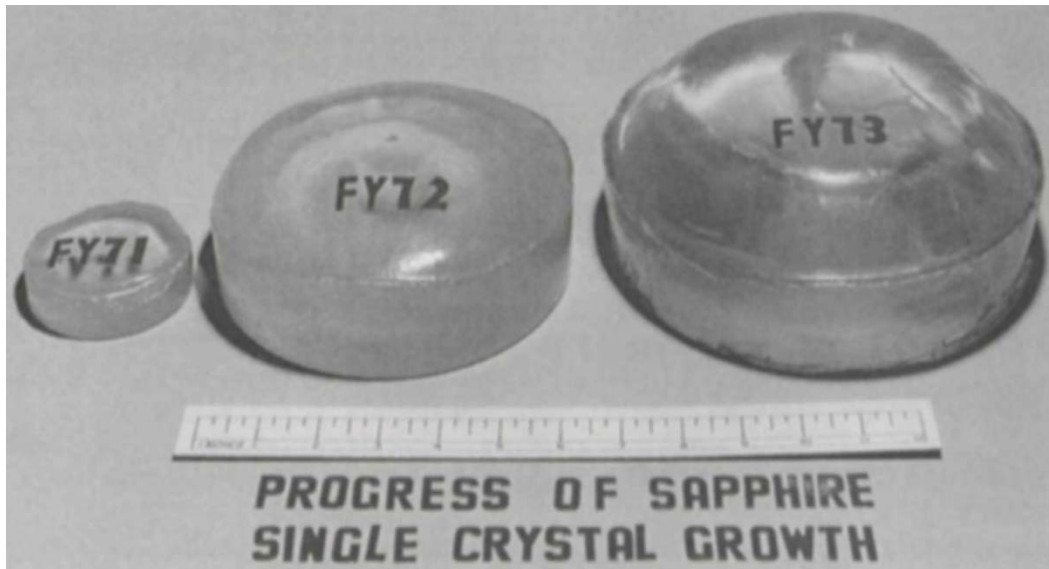
Crystals grown 1972/73 were largest diameter sapphire ever grown at that time

Window made from 6″ diameter hexagons

Origin of Crystal Systems, Inc as told by Fred Schmid

- "By early 1971 I was convinced that the…Schmid-Viechnicki Technique…was a breakthrough and felt that I would need to find a market for sapphire"

- Interest in sapphire was expressed by Inselec and Insaco for SOS (silicon-on-sapphire)

- Schmid convinces sailing buddy, Larry Ingber, and accountant, Dick Kanter, to invest in Crystal Systems, in which Schmid would hold 51% interest

- July 1971: Schmid purchases scrapped CVD furnace from Raytheon for $1750

- Aug 1971: Crystal Systems incorporated. Schmid works on furnace in his garage

- Furnace moved into space at Shetland Industrial Park in Salem

- "All this time I still had my job at AMRL and was working…between 18 and 20 hours a day"

- July 1972: 6″ boule grown and 2″ cores drilled for SOS wafers. "All the boules were stressed and loaded with gas near the outside periphery because I didn't understand the growth process."

- Sept 1972: Schmid leaves AMRL to work full time with 1 helper "just getting out of high school." 1st year sales <$50K to Inselec and Insaco

- Sept 1973: CSI hires 1st full-time employee; Judy Schmid handles advertising

Fred Schmid's Story, continued

- "I sent our first advertising piece out as a news release…and shortly after it was published (mid-1974) I got a letter from Union Carbide indicating I was infringing on their patent and offering to license their [Czochralski] technique to me."

- 1975: CSI obtains patent for bubble-free sapphire and names technique "Heat-Exchanger Method" because of unique controllable heat exchanger

- 1973-78: Schmid develops Fixed Abrasive Slicing Technique for cutting sapphire wafers with diamond abrasive on a blade combined with rocking workpiece

- 1974: NASA selects HEM sapphire for satellites because of low optical scatter

- 1975: CSI gets government contract to grow silicon by HEM

- 1977: Chandra Khattak hired from Brookhaven to work on Si. 1st crack-free silicon grown by HEM

- 1978: CSI moves to current quarters and grows 1st 12″ boule

- 1979: SBIR program initiated and CSI gets one of 1st contracts for laser-quality ruby

- 1980-82: HEM Si for photovoltaics

- 1987-89: Ti:sapphire commercialized

Crystal Systems
Management in 1996

Peggy Mulane, Vicky Herman,
Fred Schmid, Chandra Khattak,
Mark Felt, Henry Rogers,
Maynard Smith

HEM Furnaces

CSI products
- sapphire
  (boules up to 15″ diameter)
- polycrystalline Si
- HEM furnaces
- crystal slicing machines
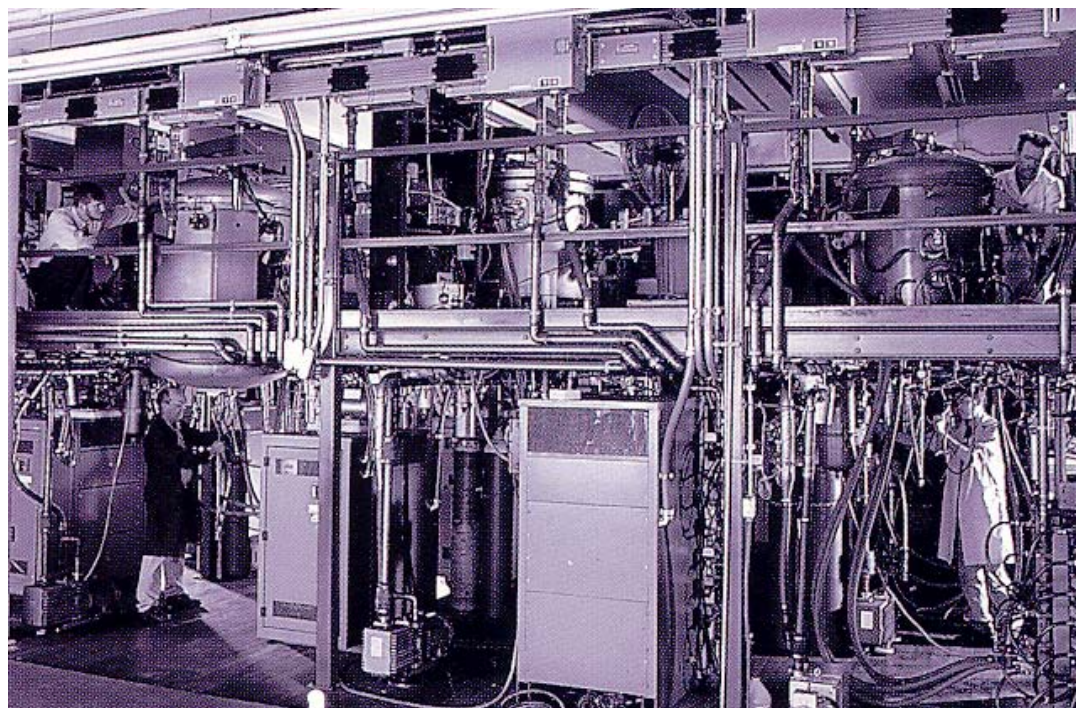
Fixed Abrasive Slicing Technique
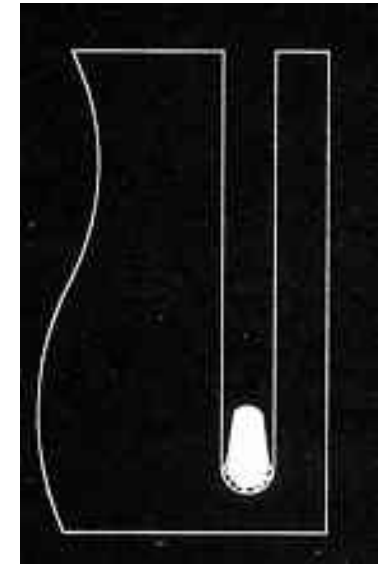
Shaped wire reduces
kerf loss to 150 μm
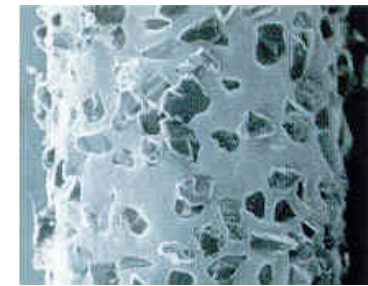
Diamond abrasive
plated onto Winter wire
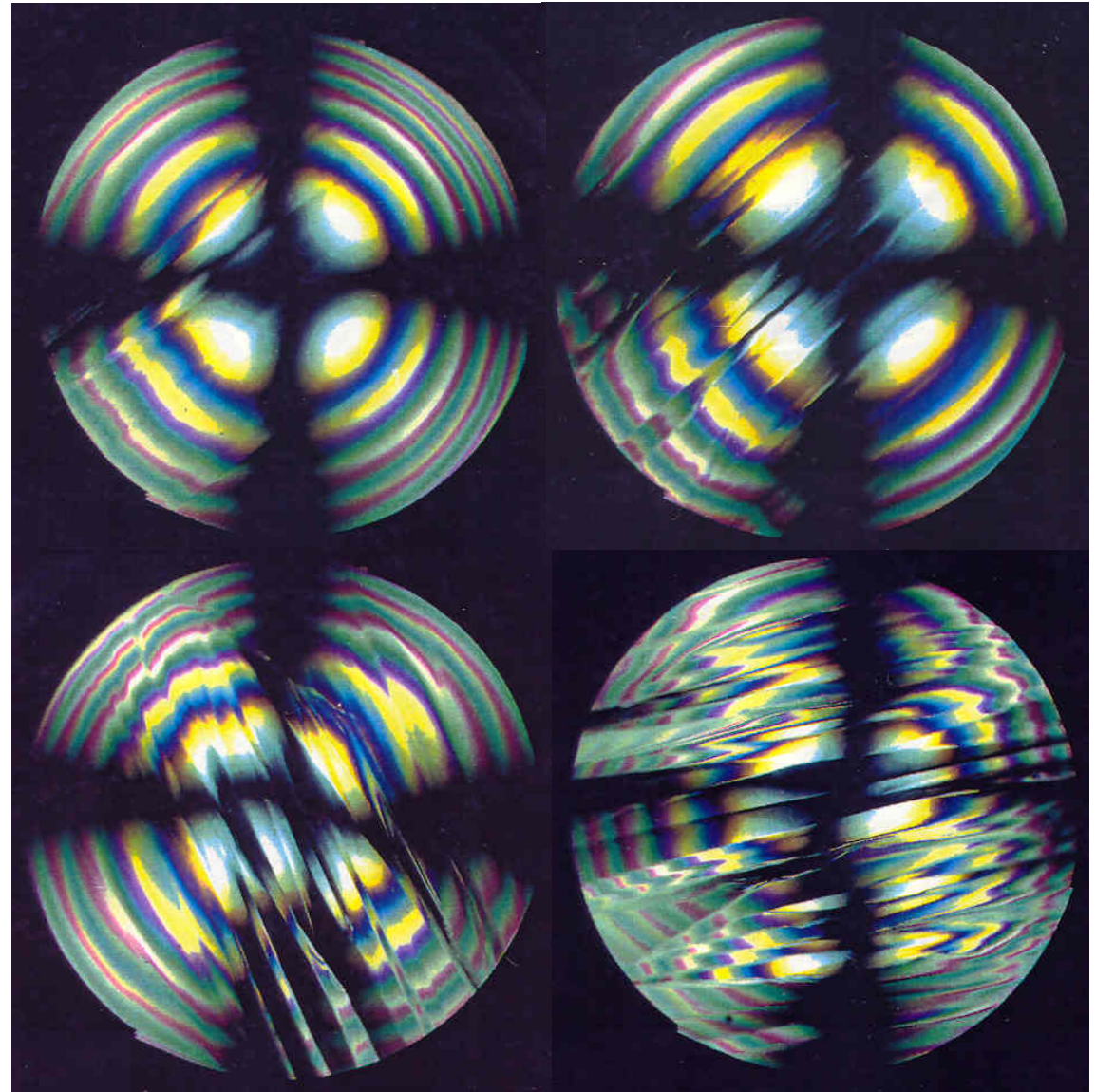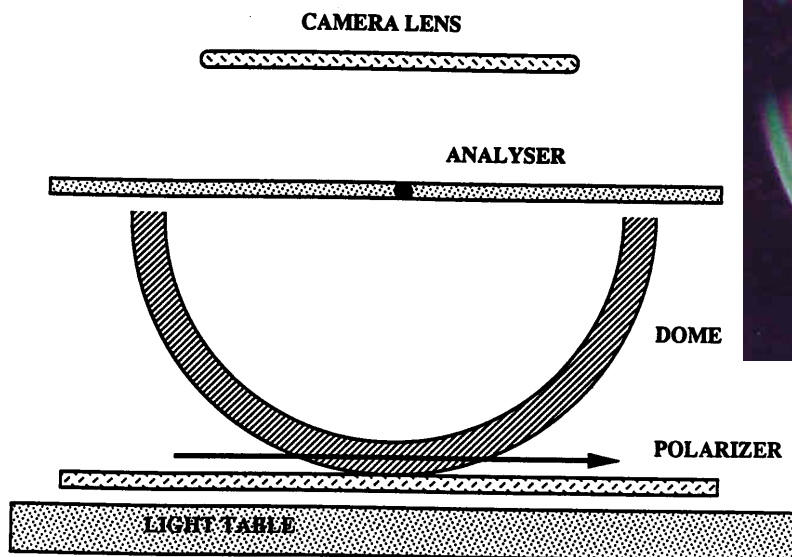
Growth of Near-Net-Shape Sapphire Domes by EFG Method

Navy manufacturing technology
Contract at Saphikon 1989–1992
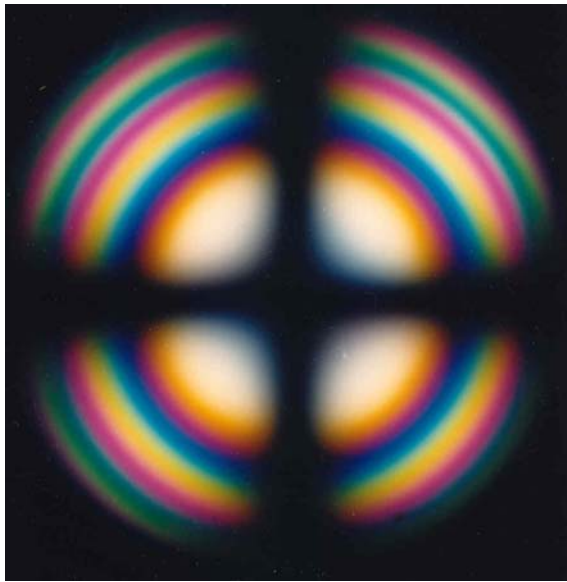
High-quality single-crystal sapphire dome viewed through crossed polarizers

CAMERA LENS

ANALYSER

DOME

POLARIZER

LIGHT TABLE

Polished EFG near-net-shape domes viewed through crossed polarizers

Growth of Near-Net-Shape Sapphire Domes by HEM Method
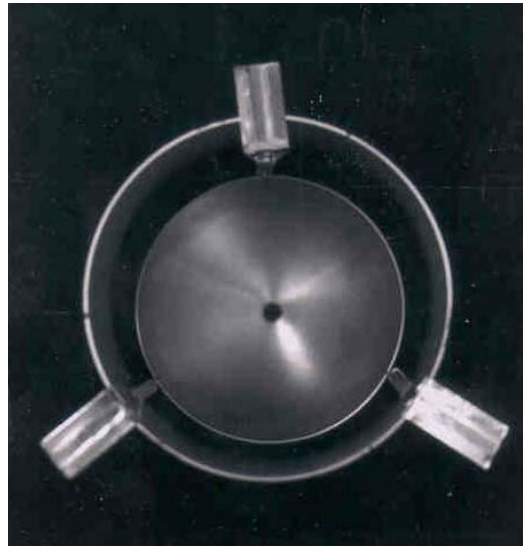
Molybdenum preforms placed in molten alumina charge for HEM growth at Crystal Systems

Navy contract 1985-86
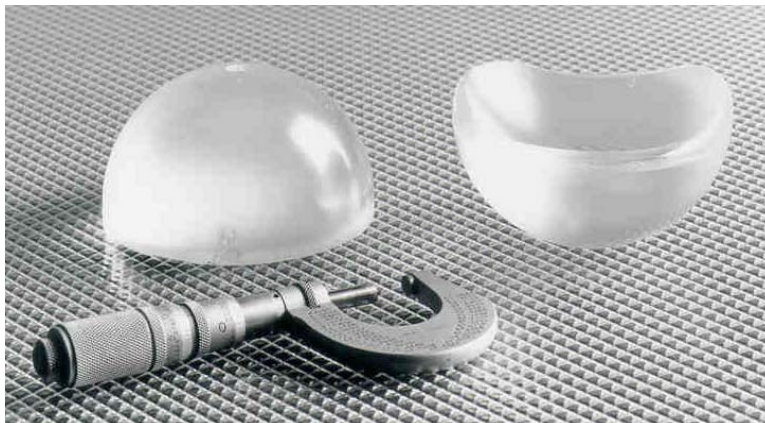
As-grown blanks

Polished dome and as-grown blank

Crystal Systems

Once upon a time, one dome was hogged out of one cylinder of sapphire

Precision Lapping and Optical Co.
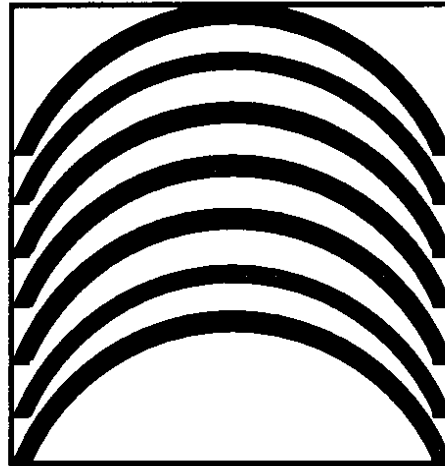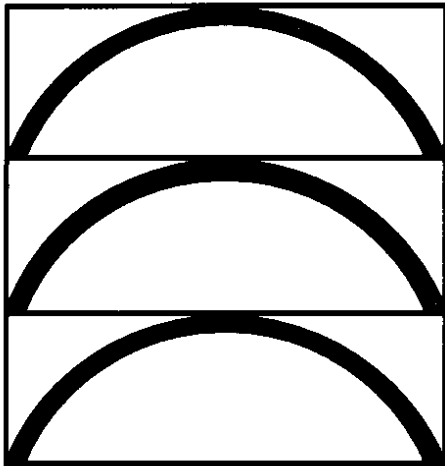
Then scooping was invented and many more domes could be taken from the same volume

Diamond-impregnated scooping tools

Scooped dome blanks

Scooping domes at Crystal Systems

- Rotate sapphire rod and scooping tool in opposite directions to cut out inside diameter with the small scooping tool whose outside edge is the active cutting surface

- Then use larger tool to cut outer diameter of the dome. Inside edge of tool is active cutting surface

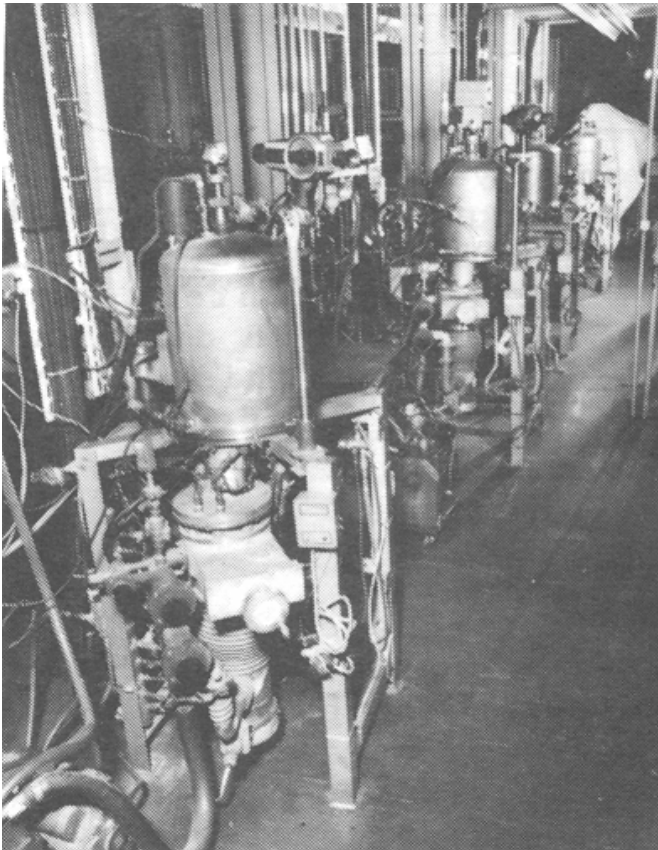- Small cylindrical plug is left at apex of dome connecting it to next dome in stack. Light force breaks domes apart at end of scooping

Pyrometer

Mo radiation shield

Crucible lid

Seed crystal

Sapphire

Mo crucible

3-phase graphite heating element

Vacuum system

Power control

Hottest

Coolest
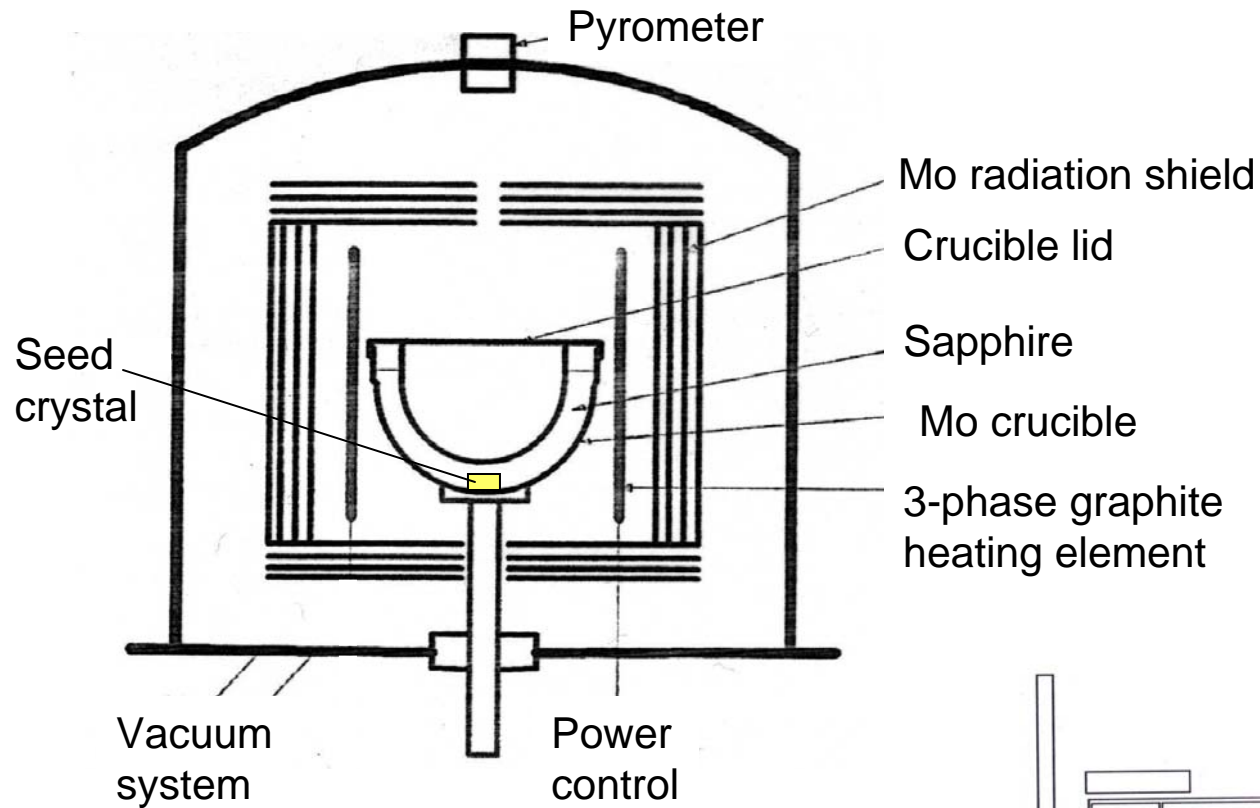
**Gradient Solidification
Sapphire Growth
at Rotem Industries, Israel**
Founded in 1969

Atara Horowitz
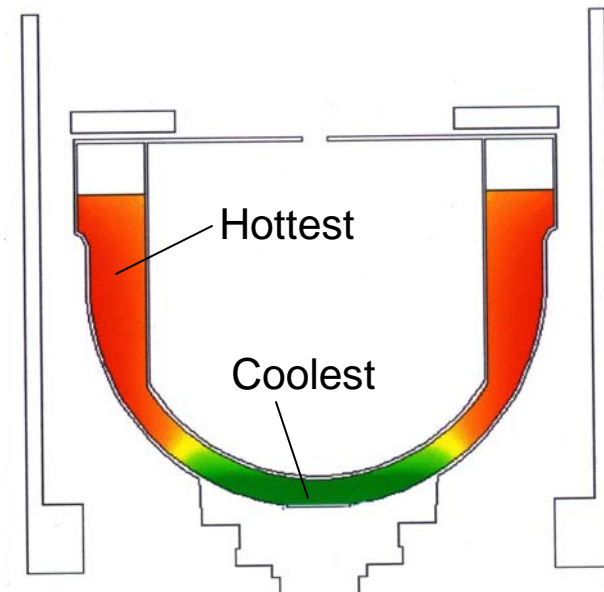
Rotem Sapphire
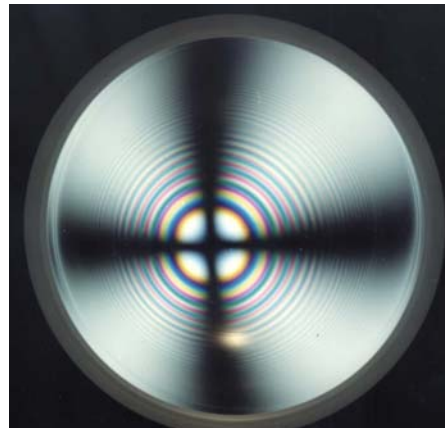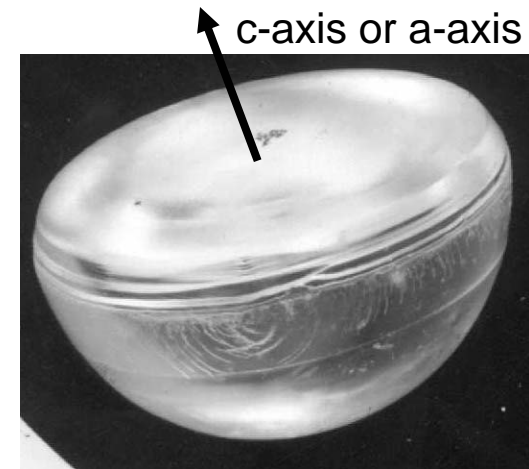

Rotem furnaces

Polished   As-grown dome

Dome through crossed polarizers

c-axis or a-axis

As-grown boule
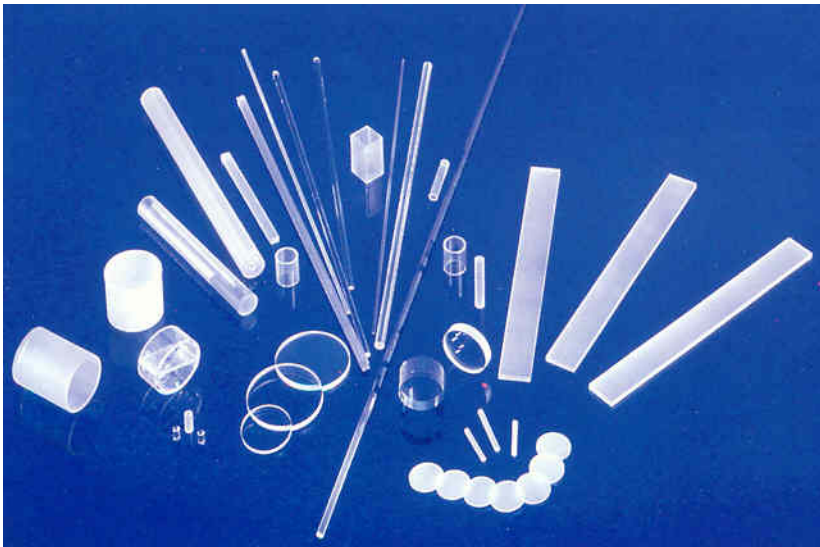

Sapphire dome
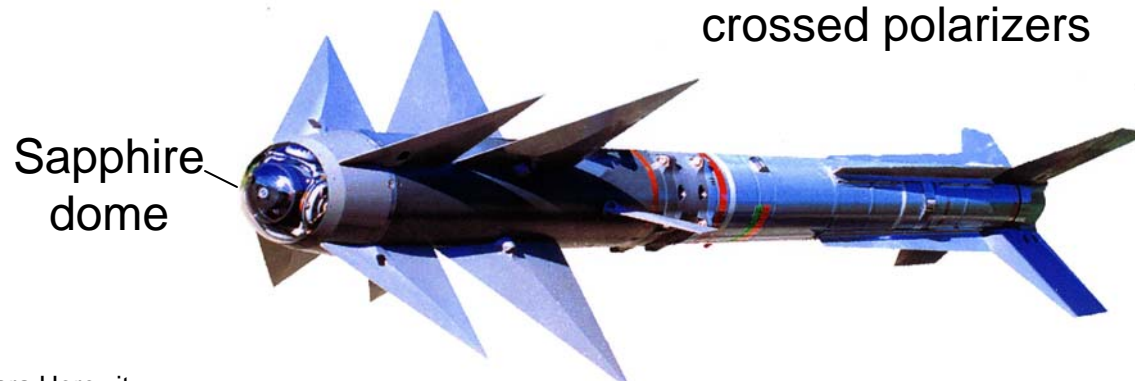
Horizontal directional solidification
(Bridgman growth)

Stepanov (EFG) growth

S & R Rubicon Sapphire
Russian American Company, Illinois

Verneuil growth

S & R Rubicon also uses
Kyropoulos growth method
for highest crystal quality

Sapphire from Atlas
Russian Research and Production Company

Kyropoulos growth method, also called GOI in Russia

JEWELLERY

USING VERNEUIL METHOD, WE PRODUCE THE WHOLE RANGE OF COLOURED CORUNDUM AND SPINEL CRYSTALS. THESE PRODUCTS COMPLY WITH THE GENERALLY ACCEPTED WORLD STANDARDS.

BLUE SAPPHIRE

Ø 40 мм

Verneuil Sapphire from Atlas
Russian Research and Production Company

55

If he didn't talk so much, he would have finished his ice cream by now